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COMPREHENSIVE TECHNICAL REPORT ON ALL ATMOSPHERIC CONTAMINANTS ASSOCIATED WITH PHOTOCHEMICAL AIR POLLUTION

Lowell G. Wayne, et al

System Development Corporation

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This document analyzes the interrelationships of contaminant, environmental and source factors involved in the total photochemical pollution system. The intent is to generalize the principles and techniques of photochemical-environmental appraisal -- developed first in Los Angeles, where this problem has been most studied -- for application to other regions of the United States. Specifically, this document analyzes illustrative applications of techniques for appraising air quality and predicting its trends. These techniques include, especially, multivariate statistical analysis of information obtained from air monitoring, and simulation modeling for studying future interactions of reactive contaminants.

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by

Lowell G. Wayne, Robert J. Bryan,
Mel Weisburd and Roy Danchick

System Development Corporation
2500 Colorado Avenue
Santa Monica, California 90406

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M. I. Weisburd
Project Manager

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CHAPTER 1

THE PHOTOCHEMICAL AIR POLLUTION COMPLEX

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A. INTRODUCTION

1. Scope

This document is a reflection of the literature on the origin and effects of a group of atmospheric contaminants known collectively as photochemical air pollution or photochemical smog. Air Quality Criteria documents currently being prepared describe available scientific information concerning the effects of numerous contaminants on health and welfare; they also provide appraisal of the environmental aspects of the problem.

This document analyzes the interrelationships of contaminant, environmental and source factors involved in the total photochemical pollution system. The intent is to generalize the principles and techniques of photochemical-environmental appraisal--developed first in Los Angeles, where this problem has been most studied--for application to other regions of the United States. Specifically, this document analyzes illustrative applications of techniques for appraising air quality and predicting its trends. These techniques include, especially, multivariate statistical analysis of information obtained from air monitoring, and simulation modeling for studying future interactions of reactive contaminants.

2. Background

While many of the causative factors of photochemical smog are well known, gaps and complexities still remain. After nearly 20 years of research, the processes underlying photochemical smog are only partially understood.

Problems remain in obtaining accurate, representative and systematically generated data that sensitively measure the effects of the parameters; in extrapolating from experimental results in static chambers to ambient conditions; and in completing information on chemical details of the photochemical system. Furthermore, methodological problems are involved in analyzing all of the concurrent factors and interactions.

Photochemical air pollution has its origin in a number of atmospheric contaminants which, through the intermediacy of solar radiation, undergo marked change in the atmosphere. The chemical change results from a complex host of individual chemical reactions, each of which proceeds at its own characteristic rate determined by factors of solar intensity, temperature, and concentration of reacting chemical entities. Most (or all) of these reactions occur simultaneously; many are interdependent; some are competitive. The primary contaminants involved in the complex--that is, those contaminants which are mainly consumed in the course of the reactions and whose presence is apparently necessary for the development of the photochemical smog complex--are certain oxides of nitrogen and a multitude of hydrocarbons and other organic gases. The organic gases vary widely in concentration and reactivity; consequently, there are wide differences in the degree of their involvement in the photochemical system.

Photochemical smog is the generic term applied to the dynamic atmospheric system at any stage of this reaction complex. It comprises not only the essential primary contaminants referenced above, but also any other primary contaminants (such as oxides of sulfur, carbon monoxide, or particulate matter) which may react with any other components of the complex, as well as a great variety of reaction products.

B. PHENOMENOLOGY OF PHOTOCHEMICAL SMOG

Photochemical smog is characterized phenomenologically by impairment of visibility, discoloration of the atmosphere, eye irritation, and damage to vegetation and property. Several of the smog constituents responsible for some of these effects have been identified, but the elucidation has not been completed. It is therefore necessary, in considering such effects, to attempt to relate them wherever possible to other parameters of the atmospheric system (such as the concentrations of primary contaminants).

1. Impairment of Visibility

Visibility reduction is one of the most commonly observed manifestations of urban air pollution. It is caused by the scattering and absorption of light by particles in the atmosphere and depends in a complicated way on the concentration and properties of those particles.

Particles are present in photochemical smog as primary contaminants from urban sources such as industrial combustion and vehicular transportation, and from natural sources such as sea and soil. Additional material accumulates on particles as a result of the smog reactions, so that the particles become larger, scatter light more copiously, and thus interfere more with visibility. This additional material, existing in the liquid state, is referred to as photochemical aerosol.

The extent of interference with visibility produced by the smog-generated aerosol depends to an unknown extent on the relative humidity of the affected air mass. One operational criterion for an adverse effect of smog, as stated by the California State Air Quality Standards, is the presence of particulate matter sufficient to reduce visibility to less than 3 miles when relative humidity is less than 70 percent. Under the climatological regime of the Los Angeles Basin, days sunny enough for photochemical smog usually have less than 70 percent relative humidity, and the aerosol gives the appearance of a thick yellowish haze. In 1967, this State Standard was exceeded in Los Angeles County on 190 days.

Despite the fact that photochemical smog is usually formed in warm, dry weather, it is not unlikely that the aerosol can persist into nighttime hours and intensify radiation fogs formed in situ in the affected air mass. Thus fog, while not a useful indication of the prevalence of photochemical smog, may be an occasional consequence of it. It is of interest to note that smog days in the Los Angeles Basin, according to the Air Pollution Control District, frequently start with fog along the coast at sunrise.

While it is clear that photochemical smog impairs visibility, it is not clear how this effect is related to the concentrations and other parameters of the photochemical complex. Studies of the chemical composition of aerosol material obtained from atmospheric sampling in 1952 showed the presence of organic compounds; these presumably were formed by the photochemical reaction system from hydrocarbons and other organic gas primary contaminants. In the inorganic portion of the particulate matter sulfates are commonly found, which may arise in part from the participation of gaseous sulfur dioxide in the photochemical reaction system. Likewise, nitrates occur, which may result from reactions involving the oxides of nitrogen. There is no information as to the importance of these aerosol constituents relative to the impairment of visibility in photochemical smog.

2. Discoloration of the Atmosphere

In episodes of photochemical smog the contaminated air takes on various colors--depending on the conditions under which it is viewed--ranging from dull blue through yellow to a dirty brown. Like the impairment of visibility, these discoloration effects are caused mostly by the light-scattering properties of particles in the atmosphere. However, one smog constituent--namely nitrogen dioxide--is a colored gas and, if present in sufficiently high concentrations and in a sufficiently extensive air mass, would be expected to color the atmosphere to orange-brown. It is not known whether the necessary conditions for observation of this phenomenon have ever existed in an ambient atmosphere, but the observed color of photochemical smog is frequently consistent with the hypothesis that nitrogen dioxide contributes significantly to its appearance. In view of this effect, quantitative estimates of the degree of coloration to be expected led the California Air Resources Board to set a nitrogen dioxide concentration of 0.25 ppm as an adverse level.

3. Eye Irritation and other Forms of Human Discomfort

Among manifestations directly affecting the human body, eye irritation is the most readily detected by people exposed to photochemical smog. In episodes of severe smog, over three-quarters of the inhabitants may observe irritation of the eyes, while a small proportion complain of irritation of nose or throat, or of chest discomfort, especially during exercise. Respondents in a survey in California, as reported by Hausknecht,[1] identified eye irritation as the most prevalent effect of air pollution. Other effects cited were nose and throat irritation, cough and sinus symptoms, discomfort or difficulty in breathing, headache, and annoyance due to odor or other qualities of the atmosphere. Presumably most of the air pollution inculpated by these respondents was photochemical in nature.

Since it was first established that eye irritation is caused by photochemical smog, much research has been expended in an attempt to identify the particular constituents responsible. These irritants have a direct effect on a large proportion of the Los Angeles population and thus have been investigated quite extensively. While studies have revealed a great deal of information concerning human response variables, they have yielded little in regard to the mechanism of irritation, nor has the identification of the chemical species responsible been completed. Some photochemical products known to cause eye irritation, however, are formaldehyde, acrolein, and peroxyacetyl nitrate.

4. Damage to Vegetation

Plant damage as a result of photochemical smog was observed in the Los Angeles area in the early 1940's and since has been found increasingly in many other places. Such damage takes many forms, both obvious and subtle. It has its economic effects on plants by reducing crop yield, marking and dehydrating the foliage of leafy crops, retarding growth, or causing outright destruction. Damage to foliage is best understood because it was noticed first, being most obvious to the naked eye. The visible injury symptoms on the leaves of plants attributable to photochemical air pollution can be divided into three categories: cell collapse with subsequent collapse and killing of tissues (acute injury); chlorosis (yellowing) or other color changes (chronic injury); and growth alteration, reduced yields and change in quality. The peculiar type of injury to leafy vegetables, ornamentals and field crops now characterized by such symptoms as banding, silvering and stippling of the leaves was first investigated by Middleton et al.[2] in 1944 in a small area of Los Angeles County. By 1950, such injury had spread over a large area of Southern California and in the San Francisco Bay Area. This kind of plant injury has also spread to many widely separated areas of the United States with increased severity and associated economic losses to both farmers and nurserymen.

Annual crop damage from photochemical air pollution has been estimated at $8 million in California and $18 million on the eastern seaboard.[3] Many crops are damaged in New York's Staten Island, e.g. begonias, tobacco, potatoes, while tobacco in Connecticut and spinach in New Jersey are being continuously destroyed. Plant damage has been most intensive in Los Angeles County--in some areas on as many as 70 percent of the days of the year.[4] Ozone, peroxyacetyl nitrates (PAN), and nitrogen dioxide are the known photochemically produced phytotoxicants. Under ordinary conditions of exposure to photochemical smog the effects of these agents cannot easily be differentiated, and it is possible that other phytotoxic agents may be present. However, laboratory investigations and controlled field exposures have provided a substantial knowledge of the effects of these particular agents.

5. Damage to Materials

Damage to structural metals, surface coatings, fabrics, and other materials is a frequent effect of air pollution. In photochemical smog, destruction is mainly attributable to oxidants of various kinds, particularly O_3, which is known to cause rapid and extensive damage to rubber and textile goods.[5] The cracking of stressed rubber was used on early studies as a measure of ozone.

6. Effects on Human Health

Toxicology has shown that photochemical smog contains substances, mainly among the secondary contaminants, which have a substantial potential to harm people and animals, and epidemiology has revealed some of the ways in which such smog adversely affects people. Toxic components include ozone, nitrogen dioxide, formaldehyde and other aldehydes, and peroxyacetyl nitrates. Doubtless many of the less abundant products, such as peroxides and alkyl nitrates, could also be characterized as toxic.

In epidemiological studies,[6] photochemical smog has been incriminated as a cause of irritation of the eyes and upper respiratory tract, of decreased efficiency in the performance of physical and mental tasks, of difficulty or discomfort in breathing, and a variety of other detrimental effects. Difficulty in breathing is experienced especially by people with preexisting respiratory impairment from emphysematous or bronchitic conditions. In guinea pigs, total pulmonary resistance is increased during photochemical smog episodes, with older animals being more severely affected.

Results of epidemiologic studies suggest that photochemical smog may evoke temporary physiological responses but little permanent effect on people in normal health. As mentioned above, asthma, emphysema and bronchitis may be exacerbated by exposure to smog. Animal experiments have shown that exposures to ozone or nitrogen dioxide may enhance susceptibility to infectious agents.

Studies of the relation of photochemical smog to death rates in California, where this type of smog has been especially well documented, reveal a substantial increase in general mortality among the aged in episodes of hot weather, usually associated with smog. High temperatures seem to be a more important causative factor than air pollution, judging by the strength of statistical association among these factors.

7. Population Reactions

The possible reactions of the public to photochemical air pollution may be understood in terms of the reactions of the Los Angeles public to this problem. The extensive number of complaints, action of citizens' groups, editorial reaction, media coverage, and the continuing notoriety and publicity given to this problem over the past 20 years attest to the extent and intensity of public attitude to this form of pollution.

While the cause of public attitudes in Los Angeles have been insufficiently studied in depth, a number of apparently obvious contributing factors can be generalized from the history of this problem:

1. The problem is dramatically visible to the entire public throughout the metropolitan area.

2. Smog haze interferes with visibility, obscures views of the mountains and sea and other familiar portions of the Los Angeles area, and produces an undesirable discoloration of the sky--even when sunny and cloudless. Smog thus clearly interferes with the enjoyment of scenic attributes that are of primary social value in the Los Angeles area.

3. Smog produces a physiological response--eye irritation (and possibly other responses)--that directly affects a significant proportion of the population.

4. The objective manifestations of smog have caused almost universal concern that smog may be damaging health.

C. Basic Concepts of Air Quality Relative to Photochemical Smog

For practical purposes, the important aspects of air quality are those that relate to the effects of air on organisms, and the senses, sensibilities, and pocketbooks of people; various such aspects have been discussed in the preceding pages. To deal quantitatively with these relations, it is necessary to study the responses of various types of sensors--human, animal, vegetable, and material--when exposed to various concentrations of contaminants for various periods of time. (The results of such studies are presented in documents known as Air Quality Criteria.) The effects to be expected in a given community as a result of impaired air quality can be predicted from estimates of the concentrations of contaminants at sensor locations. These concentrations, in turn, can be estimated if enough detail is known concerning locations of the sources of contaminants and the variables governing their distribution in the atmosphere.

For contaminants which undergo no chemical change after being emitted into the atmosphere, methods of estimating concentrations are based mainly on certain straightforward simplifications of recognized principles of atmospheric transport, assuming that contaminant molecules are indestructible. For reacting contaminants or for contaminants formed by reactions in the atmosphere, concentrations cannot be predicted unless chemical behavior is considered. Thus, the estimation of contaminant concentrations and the prediction of the effects of those contaminants on the sensors within a community or region are more complicated and difficult for reacting contaminants than for those which are chemically inert.

In the photochemical air pollution complex some of the effects are related to the history of concentrations of the emitted contaminants, which are reduced by their involvement in atmospheric chemical reactions; other effects are related to concentrations of contaminants which are generated in the atmosphere by those same reactions. Reliable prediction of the effects of these newly generated contaminants can only be accomplished if the chemistry of the atmospheric reactions is understood in sufficient detail.

In the photochemical air pollution complex, most of the atmospheric reactions are insensitive to light and take place on any suitable encounter of a pair of reacting species. However, certain key reactions--known as photochemical reactions--proceed only in the presence of light, and convert the energy of the light into chemical energy which, as a consequence, essentially fuels all the chemical changes which occur in the contaminated atmosphere.

In the ensuring discussion, contaminants will be referred to as "primary" or "secondary" mainly on the basis of whether they are reactants consumed, or products generated by the atmospheric reactions. Primary contaminants according to this definition include: all organic vapors and gases entering the atmosphere, except for a few believed unreactive; nitric oxide and nitrogen dioxide; and various adventitious contaminants such as sulfur dioxide, carbon monoxide and possibly others (gas, vapor, or aerosol). Secondary contaminants are any products of reactions involving the primary contaminants. (These include some compounds also eligible as primary contaminants, especially nitrogen dioxide). Among the secondary contaminants are some chemical species of uncertain chemical identity, sometimes detectable by chemical or physiological effects, and quantifiable only by such effects (if at all).

A schematic illustration depicting the principal components of the photochemcial air pollution problem is shown in Figure 1-1. Reactive contaminants are introduced into the system by various categories of human activities (sources). The contaminants are then subject to the actions of the atmospheric environment and solar radiation with respect to transport accumulation and dispersal and the enhancement or retardation of chemical reactions. The effect of air pollution is determined by its influence on receptors--human, animal, biological, and material.

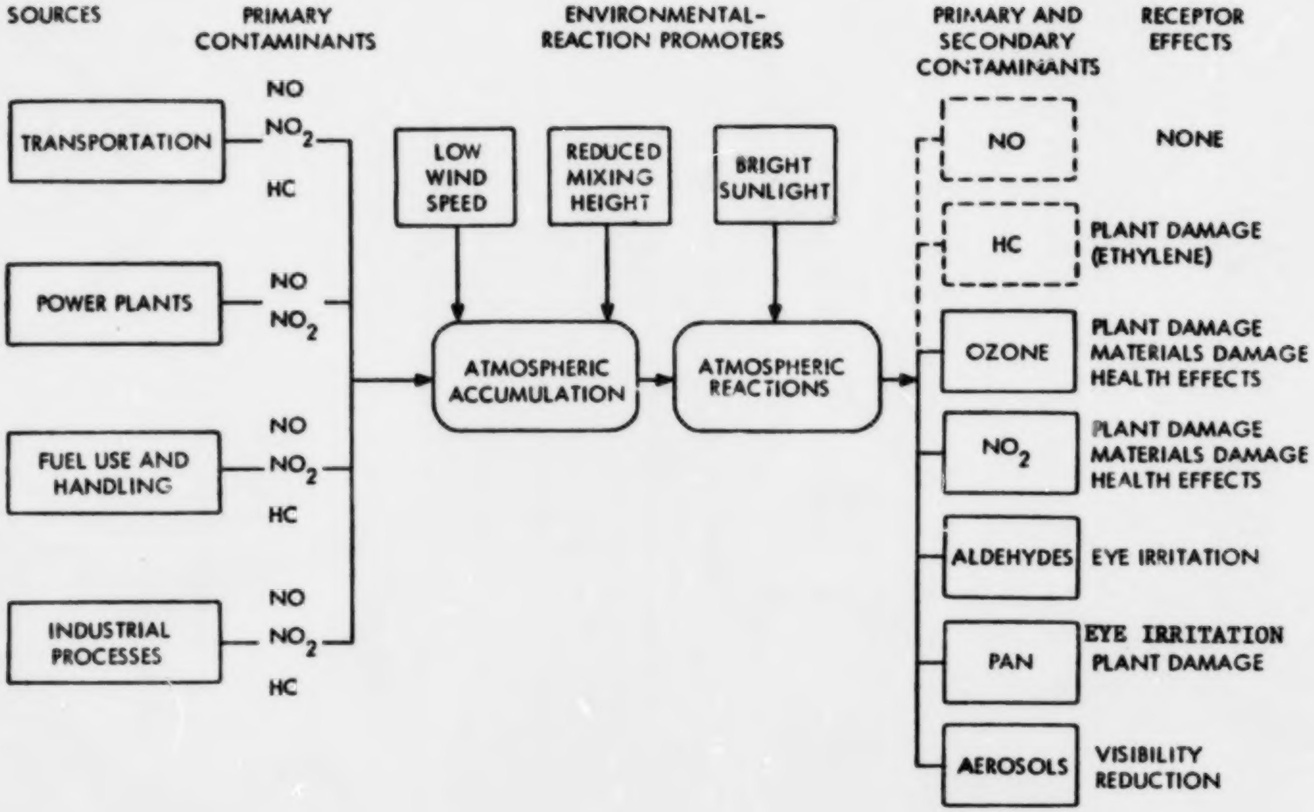

Figure 1-1. GENERALIZED SCHEME OF PRINCIPAL COMPONENTS OF THE PHOTOCHEMICAL AIR POLLUTION SYSTEM, ILLUSTRATING THE RELATIONSHIP BETWEEN SOURCES, SECONDARY CONTAMINANT EMISSIONS, ATMOSPHERIC REACTIONS, PRIMARY (IN BROKEN BOXES) AND SECONDARY CONTAMINANT OUTPUTS AND RECEPTOR EFFECTS.

In the production of smog the atmosphere acts as a chemical reactor with inputs of materials and energy. The contents of the atmospheric reactor are transformed by the action of sunlight into the irritating and damaging products characteristic of photochemical smog. Inputs to the atmospheric system, termed primary contaminants, are oxides of nitrogen (principally nitric oxide (NO)) from automobile exhaust and stationary sources, and organic gases (mainly hydrocarbons) from automobile exhaust. The vast supply of molecular oxygen in the air plays an important role in smog reactions; other pollutants, such as sulfur dioxide and carbon monoxide, may participate in these reactions to a minor extent. Materials produced by atmospheric reactions are termed secondary contaminants; as such, they are responsible for most of the effects associated with photochemical smog.

The air and pollutants in the atmospheric system move with various velocities and mix at various rates, depending on topography and atmospheric heating as well as other weather variables. Several factors affect reaction rates among various species: the sunlight intensity; the temperature; and the degree of mixing that takes place once primary contaminants are introduced into the atmosphere. The variety of intermediate and final products formed is quite large, including nitrogen dioxide (NO_2), ozone (O_3), aldehydes, ketones, organic hydroperoxides, peroxacetyl nitrates, aerosols, and a number of free radicals not experimentally measured but known to be intermediates in the chemical reactions.

Convection and dispersion have a significant influence on photochemical smog reactions, since reaction rates depend on concentrations which are, in turn, considerably affected by atmospheric mixing. Roughly the same quantity of primary contaminants is poured into the air of a city every weekday, the smog severity being determined by prevailing meteorological conditions. In particular, photochemical smog formation is favored by light winds and intense sunlight and by temperature inversions, which prevent mixing between the lower and upper levels of the atmosphere.

As illustrated in Figure 1-2 and discussed below, contaminants in typical Los Angeles smog episodes follow a fairly consistent pattern:

- Predawn. During the predawn hours of the morning, the concentrations of primary contaminants, NO and hydrocarbons* increase slowly in the absence of wind. The secondary contaminants, O_3 and NO_2, remain at low levels. (Before sunrise, the ratio of concentrations of NO_2 to NO may be one-tenth or less.)
- Morning. As the sun rises, and with the injection of large quantities of NO and hydrocarbons from morning traffic, NO_2 is generated at a substantial rate. The NO appears to convert rapidly and almost quantitatively to NO_2. When the NO is

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*In addition to its technically correct chemical usage, the term "hydrocarbon" may be used in this document to include other organic gases.

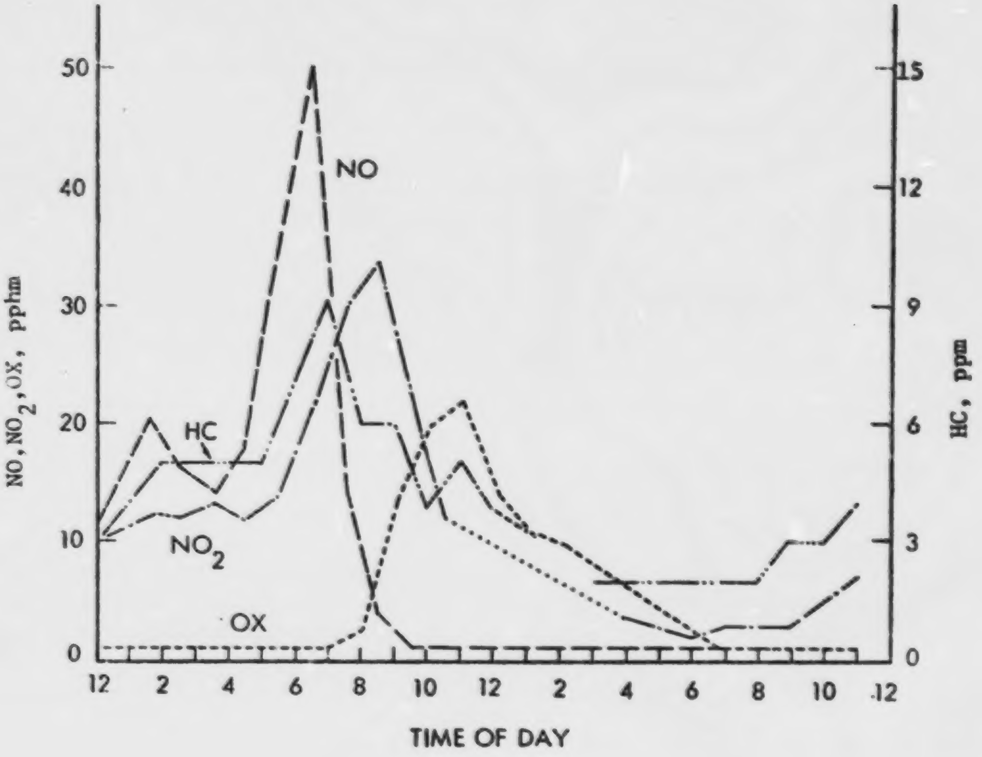

Figure 1-2. DIURNAL VARIATION IN HOURLY AVERAGE CONCENTRATION FOR EACH HOUR FOR FOUR CONTAMINANTS MEASURED AT DOWNTOWN LOS ANGELES--SEPTEMBER 3, 1964.

almost fully converted to NO_2, O_3 begins to appear, accumulates until sometime after noon, and then gradually declines. As the concentration of O_3 increases, the concentration of NO_2 decreases from its peak attained in the morning.

- Late Afternoon. The late afternoon traffic injects a fresh supply of NO and hydrocarbons into the atmosphere. However, high concentrations of contaminants are not usually seen at this time, largely because of dilution and displacement of air by the sea breeze.

1. Primary Contaminants

The major classes of contaminants emitted into contemporary urban atmospheres are: (1) carbon monoxide; (2) particulate matter; (3) oxides of sulphur; (4) oxides of nitrogen; and (5) organic gases. Of these, the oxides of nitrogen and organic gases are chiefly responsible for photochemical smog, while the other contaminants participate in minor ways.

Principal sources of the primary contaminants of photochemical smog in most cities (as indicated in Figure 1-1) are automobile exhaust and power plant effluents, with smaller quantities of effluents arising from industry and other sources. Because gasoline combustion in the internal combustion engine is usually less than 100 percent efficient, minor quantities of the original fuel, partially oxidized fuel and unsaturated hydrocarbons are exhause constituents, along with CO_2 and H_2O. In addition, nitrogen and oxygen of the air combine chemically as in all high-temperature combustion processes to form NO. Automobile exhaust also contains particulate matter, emitted at rates of billions of particles per second. Particulates serve as condensation nuclei for atmospheric aerosols, which may further contribute to the haze manifestations of photochemical smog.

Specific primary contaminants frequently function in a dual capacity. Certain hydrocarbons, the oxides of nitrogen, and the oxides of sulfur are undesirable pollutants in themselves in addition to participating in chemical reactions which produce additional undesired byproducts.

2. Atmospheric Reactions

Photochemical smog is produced by reactions involving NO, NO_2, organic gases and oxygen. The smog formation process is chemically characterized by: (1) oxidation of NO to NO_2, (2) oxidation of organic gases to oxygenated compounds, such as aldehydes and ketones, and (3) eventual accumulation of ozone and other oxidants.

It has been firmly established that the near-ultraviolet fraction of sunlight is necessary to the formation of photochemical smog. Detailed consideration of the components of urban atmospheres isolates NO_2 as the usual major absorber of the effective fraction of sunlight energy. The result of this absorption is the photodissociation of NO_2, yielding nitric oxide and oxygen atoms:

$$NO_2 + h\nu \rightarrow NO + O$$

The oxygen atoms react predominantly with molecular oxygen, O_2, to form O_3,

$$O + O_2 + M \rightarrow O_3 + M$$

where M is a third body (any other molecule in the system). NO and O_3 react rapidly to regenerate NO_2 and O_2,

$$NO + O_3 \rightarrow NO_2 + O_2$$

Each of these reactions is extremely fast--at least an order of magnitude faster than other reactions occurring in the atmosphere. There are several other reactions involving NO, NO_2, O_2, O_3 and other oxides of nitrogen, but these three are generally regarded as the most important. Stephens[7] has calculated the O_3 concentration that might be formed at steady state by irradiating any mixture of NO, O_3, NO_2 and O_2 in the absence of other species. He estimates that 10 pphm of NO_2 in air could yield 2.7 pphm of O_3, together with the same concentration of NO in each case. This calculation was based on initial zero NO, and these O_3 concentrations are still far below those sometimes found in polluted urban air. In fact, most of the oxides of nitrogen are emitted as NO which, when present, prevents any appreciable O_3 concentration from being reached as a result of these reactions. Thus, other reactions must be contributing to the smog formation process.

A process which is slow compared to these reactions but which converts NO to NO_2 without consuming an equivalent amount of O_3 can lead to the accumulation of O_3. The presence of reactive hydrocarbons provides such a process. Both O and O_3 have the ability to react with the oxidize hydrocarbons. The intermediates formed in such reactions are highly reactive and readily participate in further reactions or decompose to yield free radicals. Free radicals, from the reaction of hydrocarbons with 0 and--in smaller quantities--from the photodissociation of aldehydes, ketones and certain other carbon compounds, are intermediates in the further reactions of the photochemical smog system.

The free radicals formed react avidly with 0_2, NO, NO_2, hydrocarbons and other free radicals. Reactions with 0_2 tend to add the oxygen to the radical to produce peroxy radicals. Reactions of the oxygen-containing free radicals with NO yield NO_2. Reactions of the free radicals with NO_2 generally yield organic nitrates. Reactions with hydrocarbons lead to larger radicals. Evidence of the reaction of hydrocarbons with 0 and 0_3 is based on the abundance of oxygen-containing products which are observed in laboratory simulations and in polluted air. Organic nitrite and nitrate products, e.g., peroxyacetyl nitrate (PAN), provide evidence for the existence of free radicals in the system.

Thus the free radicals participate in a chain reaction mechanism initiated by the reactions of hydrocarbons with 0 and 0_3; propagated by the reactions of radicals with 0_2, NO, and fresh hydrocarbons; and terminated by their reactions with NO_2 and other radicals. The key aspect of the chain reactions process is that formation of one free radical, for example, from the reaction of 0 and a hydrocarbon, will result in many propagation steps before termination. A typical history of one such radical might be reaction with NO to give NO_2 and another radical. This radical then combines with 0_2

to replenish the oxygen lost to NO. The oxygenated radical then participates in a reaction with another NO molecule to generate NO_2, resulting in many molecules of NO converted to NO_2 for each free radical formed. This process provides the alternate path for oxidation of NO to NO_2 and subsequent accumulation of O_3. The termination steps in the chain reaction explain the existence of many of the oxygen-containing organic products found in polluted air.

The oxidation of nitric oxide is thus clearly a major consequence of photochemical smog reactions. At the same time, other contaminants which happen to be present in the atmosphere are subject to possible chemical reactions with the reactive intermediates produced by these reactions. In particular, it is likely that small fractions of sulfur dioxide and carbon monoxide, when present, may be oxidized. In the case of sulfur dioxide, resulting products are to be found mainly in the aerosol form. The chemistry of these reactions has not been elucidated; their consequences would appear to be minor with the sole exception of the probable effect of the sulfur-containing products in causing atmospheric turbidity, thereby reducing visibility.

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CHAPTER 2

SOURCES, PRINCIPLES OF CONTROL, AND NATURE OF PHOTOCHEMICAL REACTANTS

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A. INTRODUCTION

The environmental appraisal of photochemical air contaminants constitutes evaluation of (1) the occurrence, behavior, and effects of hydrocarbons, nitrogen oxides and their reaction products in the atmosphere (summarized in the previous chapter), and (2) the nature, location and relative importance of their sources. This chapter provides a basic familiarization with the sources of photochemical pollution, the chemical and physical properties of the pollutants, and the principles of control.

Air pollution can result from numerous processes--natural or technological. From the standpoint of environmental appraisal these processes can be viewed as taking place in two stages. The first consists of the input of contaminants to the atmospheric system. Knowledge of contaminants emitted and their emission rates is sufficient for the purposes of environmental appraisal. The second stage--leading to control implementation plans--is more difficult. Here, the numerous factors influencing pollution output that are subject to control must be determined. These include the design, performance, and operation of equipment as well as demographic, behavioral, and economic factors that determine fuel consumption, production rates, and temporal emission patterns. These factors are discussed briefly in this chapter and treated extensively in the Control Techniques documents for stationary sources of hydrocarbons and nitrogen oxides and in a separate document on the control of nitrogen oxides, hydrocarbons, and carbon monoxide from mobile sources, published by the National Air Pollution Control Administration.

B. NATURAL SOURCES AND BACKGROUND LEVELS OF PHOTOCHEMICAL REACTANTS

1. Hydrocarbons

The presence of natural hydrocarbons in the atmosphere, particularly methane, has been established by measurement only recently.[1] Although most of these hydrocarbons arise from biological sources, small and highly localized quantities of methane and a few other lower molecular weight hydrocarbons are attributable to geothermal areas, coal fields, natural gas and petroleum fields, and natural fires.

Various estimates have been made of the contributions of these natural sources to hydrocarbons in the atmosphere. Koyama has estimated the production rate of methane to be about 3×10^8 tons per year.[2] Of this amount the greatest quantity arises from the decomposition of organic matter at the earth's surface. Ehhalt,[3] however, concludes that this is a very conservative estimate, since methane generated in swampy areas was not included.

Volatile terpenes and isoprene constitute a separate class of hydrocarbons for which worldwide natural emission rates have been estimated. Rasmussen and Went have estimated the rate of production of such compounds to be about 4.4×10^8 ton per year.[4] Hazes associated with vegetation in many areas of the world, such as the blue haze of the Appalachian, have been ascribed to aerosol formation caused by these substances.

From these estimates it appears that production of methane from natural sources is roughly equivalent to that of the higher molecular weight volatile organics. There is a great difference, however, in natural background levels, implying a related difference in the lifetimes of these materials in their global cycles.

There is substantial agreement on the natural background of methane in the atmosphere based upon different measurement principles and locations of such measurements. Junge indicates that the worldwide range is 0.8 to 1.1 mg/m^3 (1.2 to 1.5 ppm).[5] This is seen both in optical measurements such as reported by Fink, et al.[6] and Goldberg and Muller,[7] and in chemical measurements generally done by gas chromatography.

From samples taken in nonurban atmospheres, Stephens and Burleson report methane values averaging 0.93 mg/m^3 (1.39 ppm) over southern California mountain areas during desert winds, and similar values for Hawaii. Ethane, ethylene and acetylene were found at 0.003 ppm or less.[8] Cavanagh, et al. found a mean methane concentration of 1.1 mg/m^3 (1.6 ppm) with butane at 0.14 mg/m^3 (0.06 ppm) at Point Barrow, Alaska,[9] while Swinnerton, et al., during an oceanographic cruise between Washington, D.C. and Puerto Rico, reported a mean methane concentration of 0.83 mg/m^3 (1.24 ppm).[10] Furthermore, these latter authors found that the methane content of ocean water was in equilibrium with that found in the atmosphere.

Lowest hydrocarbon measurements in the urban atmosphere, including special gas chromatographic measurements by Altshuller, et al.[11,12] and total hydrocarbon measurements by flame ionization analyzers such as those provided by the National Air Surveillance Network, the State of California SCAN network, and the Los Angeles County Air Pollution Control District, are in the same range as the values reported above for methane in nonurban areas.

Fewer measurements of other low molecular weight hydrocarbons have been made as compared to methane in nonurban areas, and no accurate statement can be given as to ranges of concentrations for these compounds. Measurements by Cavanagh, et al. on butane at Pt. Barrow, Alaska[9] and by Stephens and Burleson in southern California mountain areas on ethane, ethene and acetylene[8] are 2 or 3 orders of magnitude lower than methane.

Higher molecular weight hydrocarbon and volatile organic concentrations have been estimated by Rasmussen and Went based upon sensitive gas chromatographic measurements of alpha- and beta-pinene.[4] These measurements average about 0.01 ppm.

Using his own methane production figures and a total instantaneous mass of 4.3×10^{15} g in the atmosphere, Koyama calculated an atmospheric average life of 20 years.[2] Ehhalt considers this an overestimate and suggests that an average life of only a few years is more likely.[3] By comparison with these estimates for methane, it appears that the lifetime of higher molecular weight natural hydrocarbons may be in the order of days to months. The principal implications relating to the reported information on abundance of hydrocarbons from natural sources would appear to be in the matter of atmospheric sampling. Methane is photochemically nonreactive, and the other hydrocarbons from natural sources are too low in concentration to be of concern in urban areas. The relatively high concentration of methane as compared to other hydrocarbons of photochemical significance from man-created sources, however, makes the use of analytical methods distinguishing methane of critical importance.

To summarize, it appears that in nonurban air background levels of methane are ordinarily in the range of 1 to 1.5 ppm, while other hydrocarbons, including various terpenes, remain at levels less than 0.1 ppm.

2. Nitrogen Oxides

Of the seven known forms of nitrogen oxides, only nitric oxide (NO) and nitrogen dioxide (NO_2) are of general significance in air pollution studies. The major sources of nitric oxide and nitrogen dioxide in the atmosphere are biologic in origin. Robinson and Robbins[13] estimate that these sources contribute approximately 370 x 10^6 tons annually, while man-made sources resulting from the fixation of nitrogen and oxygen in high temperature combustion amounts only to 50 x 10^6 tons, or about 14 percent of the total.

Relatively few data are available on nitrogen oxides from nonurban areas and these are rather scattered geographically. Lodge and Pate[14] found average values of NO_2 in Panama ranging from 1.8 μg/m^3 (0.9 ppb) during the dry season to 7.1 μg/m^3 (3.6 ppb) during the rainy periods. Individual samples reached 12 μg/m^3 (6 ppb). Junge[15] reported NO_2 concentrations averaging 1.8 μg/m^3 (0.9 ppb) in Florida and 2.5 μg/m^3 (1.3 ppb) in Hawaii.

In the Rocky Mountain area of Colorado (Pikes Peak), Hamilton[16] reported an average concentration of 8.0 μg/m^3 (4.1 ppb) for NO_2 and 3.3 μg/m^3 (2.7 ppb) for NO. Ripperton, et al.[17] found an average concentration of 9.0 $\mu g/m^3$ (4.6 ppb) NO_2 in the Appalachian area of North Carolina. From these data Robinson and Robbins[13] have concluded that continental average levels of NO_2 are about 8 $\mu g/m^3$ (4 ppb) and those over ocean areas about 4 $\mu g/m^3$ (2 ppb).

Robinson and Robbins[13] have also prepared a tentative simplified global nitrogen circulation pattern in which the nitric oxide and nitrogen dioxide discharged to the atmosphere from whatever the source are primarily scavenged by hydrolysis with water. The end products formed are nitrates. Based upon the estimated global background levels and on the previously cited annual input rates to the atmosphere, the average residence time for nitrogen dioxide is about 3 days.

Several conclusions on background levels and the natural cycle of nitrogen compounds can be drawn from the above information. First, the natural sources of nitrogen oxides have little significance as related to the urban pollution problem. Second, the mean residence time of nitrogen dioxide in the atmosphere, 3 days, is too long to influence photochemical reaction and transport processes taking place over a few hours.

C. NATIONAL AND REGIONAL EMISSION LEVELS

1. Hydrocarbons

Based upon Public Health Service estimates, total nationwide emissions of hydrocarbons and related organic compounds to the atmosphere for the year 1968 amounted to approximately 27 x 10^6 tons. Table 2-1[18] shows the distribution of this total by major source categories, including percent of relative contribution. Motor vehicles (47 percent), industrial processes

Table 2-1. SUMMARY OF NATIONWIDE HYDROCARBON EMISSIONS, 1968.[18]

	Hydrocarbon Emissions	
Source	10^6 tons/year	Percent of Total Emissions
1. Transportation	13.69	51.6
a. Motor Vehicles	12.55	47.4
1. Gasoline	12.18	46.0
2. Diesel	0.37	1.4
b. Aircraft	0.34	1.3
c. Railroads	0.27	1.0
d. Vessels	0.20	0.7
e. Non-highway use motor fuels	0.33	1.2
2. Fuel Combustion-stationary	0.75	2.8
a. Coal	0.19	0.7
b. Fuel Oil	0.11	0.4
c. Natural Gas	Negligible	Negligible
d. Wood	0.45	1.7
3. Industrial Processes	3.76	14.2
4. Solid Waste Disposal	1.48	5.6
5. Miscellaneous	6.84	25.8
a. Forest Fires	2.18	8.2
b. Structural Fires	0.10	0.4
c. Coal Refuse	0.20	0.8
d. Organic Solvent Evaporation	3.16	11.9
e. Gasoline Marketing	1.20	4.5
TOTAL	26.52	100.0

(14 percent), and solvent usage (12 percent) constitute the most significant sources by far. According to Mason, Ozolins and Morita,[19] who reported similar information for the year 1966, approximately 63 percent of the total hydrocarbon emissions arises from urban areas.

Hydrocarbon emission estimates have been made for 22 major metropolitan areas in the United States.[19] Although information is still quite fragmentary, emissions by area range from 50,000 to 1.3 million tons per year. Table 2-2 shows this information for each of the available areas, including rates per capita and per unit area.

Perhaps of more importance are the data in Table 2-3, which provide estimates of the average and the range of contributions by source category in the 22 metropolitan areas included in the study referenced above.[19] The most significant finding was that while transportation sources accounted for a higher proportion of total hydrocarbon losses in these metropolitan areas than in the nation as a whole, the range was extremely wide: 37 to 99 percent.

2. Nitrogen Oxides

Recent estimates of total national emission levels of nitrogen oxides have changed from approximately 14×10^6 tons per year in 1966[20] to over 18×10^6 tons per year in 1968.[18] Table 2-4 shows the distribution of the latter total by major source categories. Relative percent contributions are also included. Over 90 percent of the total emissions result from the fixation of nitrogen in combustion processes and less than 2 percent from industrial processes. As with hydrocarbons, transportation at 47 percent

Table 2-2. **SUMMARY OF HYDROCARBON EMISSIONS FROM METROPOLITAN AREAS[a] IN THE UNITED STATES, 1967-1968[19].**

			Emissions		
AREA	POPULATION	AREA, mi.^{2}	10^3 Tons/yr.	Tons/Mi^2/yr	Tons/yr/1000 POP
Dayton	880,000	2310	64	28	73
Pittsburgh	2,520,000	3050	95	31	38
St. Louis	2,410,000	4500	330	73	137
Boston	2,700,000	1280	87	68	32
Cincinnati	1,660,000	2620	55	21	33
Seattle	2,010,000	15000	170	11	85
Philadelphia	5,500,000	4590	470	102	85
Birmingham	750,000	1120	64	57	85
Washington, D.C.	2,700,000	2270	310	137	115
Los Angeles	7,100,000	41000	1270	31	179
Buffalo	1,300,000	1470	130	88	100
Louisville	840,000	1390	46	33	58
San Francisco	4,500,000	7000	790	112	176
Indianapolis	1,050,000	3080	74	24	70
Hartford	2,290,000	2650	120	45	52
Milwaukee	1,730,000	2630	83	32	48
Kansas City	1,230,000	3200	230	72	187
Detroit	4,090,000	2680	480	179	117
Providence	1,200,000	1000	54	54	45
Houston	2,000,000	7800	292	37	146

[a] Defined on the basis of Standard Metropolitan Statistical Areas; these may include substantial areas which are rural in nature and thus of low population density.

Table 2-3. HYDROCARBON EMISSIONS BY SOURCE CATEGORY FOR 22 SELECTED CITIES.[19]

Source Category	Emissions (Percent of Total)
I. Transportation	
Average	70.2
Range	37-99
A. Motor Vehicles	
Average	66.9
B. Other	
Average	3.3
II. Fuel Combustion	
Average	2.8
Range	0-18
A. Power Plants	
Average	0.1
B. Industrial	
Average	2.2
C. Domestic	
Average	0.5
III. Process Losses	
Average	19.9
Range	1-63
IV. Refuse Disposal	
Average	7.1
Range	0.4-26

Table 2-4. A SUMMARY OF NATIONWIDE NITROGEN OXIDE EMISSIONS.[18]

Source Category	NO_x Emissions (10^6 tons/yr)	Percent of Total Emissions
I. Transportation	8.71	47.2
A. Motor Vehicles	7.59	41.1
1. Gasoline	6.99	37.9
2. Diesel	0.60	3.2
B. Aircraft	0.04	0.2
C. Railroads	0.43	2.3
D. Vessels	0.29	1.6
E. Nonhighway use of motor fuel	0.36	1.9
II. Fuel Combustion in Stationary Sources	7.45	40.4
A. Coal*	3.85	20.9
B. Fuel Oil *+	1.55	8.4
C. Natural Gas	1.80	9.8
D. Wood	0.25	1.3
III. Solid Waste Disposal	0.68	3.7
IV. Industrial Processes	0.20	1.1
V. Miscellaneous	1.40	7.6
Total	18.44	100.0

---

* For 1967

+ Includes kerosene and LPG

constitutes the largest single source of nitrogen oxides. Fuel combustion in stationary sources at 40 percent is next in importance, with approximately half of that amount originating from fossil-fueled electric-generating plants.

The 1966 study by Mason, et al.[19] on sources of emissions in 28 major metropolitan areas shows that a relatively wide range exists in percent of contribution by source. Data on nitrogen oxides available from 22 cities only are summarized in Table 2-5.

D. TECHNOLOGICAL SOURCES OF HYDROCARBONS AND NITROGEN OXIDES

Hydrocarbons and nitrogen oxides, along with carbon monoxide, have in common the automobile engine as a major source of community air pollution. At this point the similarity ends. Hydrocarbons originate primarily from the inefficient combustion of fuels--especially the more volatile ones, such as gasoline--with the remaining major sources including industrial process losses, solvent evaporation, and the storage, transport, and distribution of gasoline.

The great majority of nitrogen oxides emissions, on the other hand, originates from the reaction of nitrogen and oxygen in air in high temperature combustion processes. Relatively small quantities, nationally, are emitted from industrial processes, although in localized cases these may make a significant contribution.

Because of the differing control strategies required in terms of engineering, economic, and legal considerations, sources of hydrocarbons and nitrogen oxides are conveniently treated in terms of moving and stationary sources. Moving sources include gasoline and diesel-powered vehicles,

Table 2-5. NITROGEN OXIDE EMISSIONS BY SOURCE CATEGORY FOR 22 SELECTED CITIES.[19]

Source Category	Emissions (Percent of Total)
I. Transportation	
Average	42.6
Range	23-74
A. Motor Vehicles	
Average	36.3
B. Other	
Average	6.3
II. Fuel Combustion in Stationary Sources	
Average	50.7
Range	10-79
A. Power Plants	
Average	23.0
B. Industrial	
Average	23.8
C. Domestic	
Average	3.9
III. Process Losses	
Average	5.2
Range	1-21
IV. Refuse Disposal	
Average	1.5
Range	0.1-1.0

railroads, and aircraft. Due to the interrelated nature of the problems, hydrocarbons and oxides of nitrogen from these sources are considered jointly. Principal stationary sources of hydrocarbons include petroleum and petrochemical operations, solvent usage, and waste-burning. Major stationary sources of nitrogen oxides include large fossil-fueled power plants, industrial and commercial process heating, industrial furnaces, incineration, and domestic heating.

1. Mobile Sources

a. Carbureted Gasoline Engines

Carbureted gasoline internal combustion engines (i.e., conventional automobile engines) emit air pollutants from four sources (see Figure 2-1): 1) engine exhaust, 2) crankcase blowby, 3) carburetor, and 4) fuel tank. According to a survey conducted on a large number of automobiles,[21] 100 percent of the carbon monoxide, 100 percent of the nitric oxide, and about 65 percent of the unburned hydrocarbons come from the engine exhaust; another 25 percent of unburned hydrocarbons escapes from crankcase blowby, with an additional 5 percent each resulting from evaporation of gasoline from the carburetor and from the fuel tank.

The quantity and reactivity (or photochemical potential) of the unburned hydrocarbons as well as the quantity of nitric oxide and carbon monoxide emitted from the automobile exhaust depend on the engine operating mode (idle, acceleration, cruising, deceleration),[22] engine parameters (compression ratio, spark advance, air-fuel ratio, etc.),[23] and fuel composition.[24]

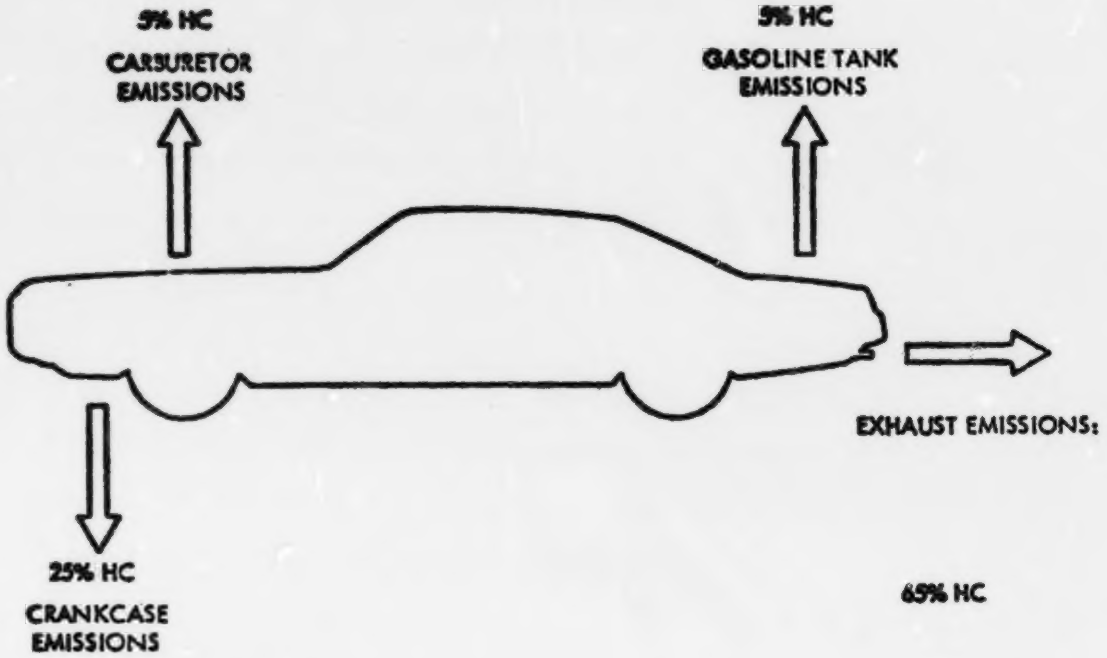

Figure 2-1. PERCENTAGE DISTRIBUTION OF HYDROCARBONS FROM THE FOUR AUTOMOBILE EMISSION SOURCES.

The concentration of the three major air pollutants in the exhaust of automobiles not equipped with exhaust emission control systems as reported in 1966 ranges as follows:

1. Total unburned hydrocarbons: 200 ppm to over 1000 ppm.
2. Carbon monoxide: 0.8 percent to over 4.0 percent.
3. Nitric oxide: 750 ppm to over 3000 ppm.

These data are based on a surveillance emission test program[25] performed according to California Standard Test Procedures,[26] 7-Mode Test Cycle, "Hot Start." For "Cold Start" the above values (except for nitric oxide) would be about 40 percent higher.

b. Diesel Engines

The emission from diesel exhaust differs from that of carbureted gasoline engines mainly because diesel fuel components are far less volatile than gasoline. Furthermore, carbureted gasoline engines, in general, operate with a deficiency of combustion air, whereas the diesel engine normally operates with a substantial excess of combustion air and a substantially higher compression ratio. Table 2-6 shows the emission factors for exhaust of carbureted gasoline engines, and Table 2-7 presents diesel engine emission factors.[27] Emission of carbon monoxide from diesel exhaust is negligible and emission of unburned hydrocarbons substantially lower than from gasoline engines. However, emission of nitrogen oxides and other contaminants is higher. Higher emission of aldehydes (and formaldehydes) is partially responsible for

Table 2-6. EMISSION FACTORS FOR AUTOMOBILE EXHAUST.

Type of Emission	Emissions	
	Pounds Per 1000 Vehicle-Miles	Pounds Per 1000 Gallons of Gas
Aldehydes (as HCHO)	0.3	4
Carbon monoxide	165.0	2300
Hydrocarbons (as C)	12.5	200
Oxides of nitrogen (as NO_2)	8.5	113
Oxides of sulfur (as SO_2)	0.6	9
Organic acids (as CH_3CO_2H)	0.3	4
Particulates	0.8	12

Table 2-7. EMISSION FACTORS FOR DIESEL ENGINES.
(pounds per 1000 gallons of diesel fuel)

Type of Emission	Emission Factor
Aldehydes (as HCHO)	10
Carbon monoxide	60
Hydrocarbons (as C)	136
Oxides of nitrogen (as NO_2)	222
Oxides of sulfur (as SO_2)	40
Organic acids (as CH_3CO_2H)	31
Particulate	110

the distinct diesel exhaust odor.[28] Emission of particulates is higher by an order of magnitude, resulting in the visible diesel exhaust smoke.[29]

Air pollution from crankcase blowby is negligible with diesel engines, since the diesel compresses only air instead of an air-fuel mixture.[28] There is practically no air pollution resulting from fuel evaporation from the fuel system, because diesel fuel has a very low volatility index.

c. Gas Turbines and Aircraft Jet Engines

The combustion process in gas turbines and aircraft jet engines differs from that of gasoline and diesel engines mainly in that it occurs at constant pressure (continuous process), low compression ratio, and with a very large excess of combustion air. In general, the exhaust emission is very low in carbon monoxide and in unburned hydrocarbons. Nitrogen oxides emission is comparable to that from gasoline engines, and emission of particulates is even higher than that from diesel engines. The first and last columns in Table 2-8 compare the emission factors of aircraft equipped with four jet engines and of aircraft equipped with four carbureted gasoline (piston) engines.[27]

Emission factors are presented on the basis of pounds per flight, where a flight is a combination of a landing and a takeoff (including taxi, takeoff, climbout, approach, and landing) that occurs below the arbitrarily chosen altitude or 3,500 feet. The main source of pollution from gas turbines and aircraft jet engines is the exhaust; pollution resulting from evaporation from the fuel tank is minimal, because fuels with low volatility are generally used.

Table 2-8. EMISSION FACTORS FOR AIRCRAFT BELOW 3500 FEET.

(pounds per flight)[a]

Types of Emission	Jet aircraft, four-engine[b, c]		Turboprop aircraft		Piston-engine aircraft	
	Conventional	Fan-jet	Two-engine	Four-engine	Two-engine	Four-engine
Aldehydes (as HCHO)	4	2.2	0.3	1.1	0.2	0.5
Carbon monoxide	35	20.6	2.0	9.0	134.0	326.0
Hydrocarbons (as C)	10	19.0	0.3	1.2	25.0	60.0
Oxides of nitrogen (as NO_2)	23	9.2	1.1	5.0	6.3	15.4
Particulates	34	7.4	0.6	2.5	0.6	1.4

[a] A flight is defined as a combination of a landing and a takeoff.

[b] No water injection on takeoff.

[c] For three-engine aircraft, multiply these data by 0.75; for two-engine aircraft, multiply these data by 0.5.

2. Stationary Sources

a. Hydrocarbon Emissions

The major stationary sources of hydrocarbons in the United States are the production, processing, storage, and transfer of petroleum products (principally gasoline) and organic solvent losses. Relatively smaller quantities arise from the combustion of fuels and refuse. A brief review of some of these sources and pertinent emission factors follows.

1) Types of Sources

Potential sources of hydrocarbon emissions in petroleum production and processing include: leakage in the oil field or refining, gasoline storage tanks, gasoline loading facilities, air blowing of asphalt, blow-down systems, catalyst regenerators, processing vessels, flares, compressors, pumps, vacuum jets, waste effluent handling equipment, turnaround operations.

Gasoline distribution and marketing systems emit hydrocarbon vapors from tank truck loading racks, service station tank-filling operations and automobile tank-filling operations.

Organic solvents are derived mainly but not exclusively from petroleum. They are used in many kinds of operations. Chemical, drug and pharmaceutical manufacturing plants can be sources of organic emissions from those operations involving the use of organic solvents. Rubber and plastic product manufacturing often involves the use of organic solvent-based adhesives and other solvent uses which lead to organic emissions. Paint and varnishes, lacquers, undercoatings, etc., are composed of 40 to 80 percent organic solvents which evaporate during or after application. Degreasing of manufactured metal items can cause significant organic emissions. Vapor phase degreasing with trichlorethylene (not a hydrocarbon) is the most widely used method, but spray degreasing with other solvents is also used. Drycleaning of clothing utilizes organic solvents and contributes to emissions. The processes by which solvents and solvent-containing materials (e.g., paints, lacquers, etc.) are manufactured are also potential sources.

Metallurgical coke plants emit varying amounts of hydrocarbons depending on type of furnace, operating methods, maintenance practices and other factors.

Fuel-burning equipment of all types can emit organics when improperly adjusted, inadequately maintained or incorrectly operated.

Waste disposal by burning can cause hydrocarbon emissions from incomplete combustion. Open burning of refuse is the greatest offense in this category. Inefficient incinerators may also be sources. Carbonaceous material from many sources is disposed of by burning.

Miscellaneous sources of organic gases from biological sources include fermentation industries, food processing, organic fertilizer processing, wood distillation and soap manufacturing.

2) Emission Factors

For individual emission sources by source type, an adequate emission inventory will define the nature, magnitude, duration, and frequency of emissions. For a regional emission inventory, detailed analysis of all sources would be desirable. It is often necessary, however, to estimate emissions from sources for which detailed data are unavailable. Estimates are derived by the use of emission factors based on sampling data, material balances, and engineering appraisals of sources similar to those in question.

Table 2-9 is a compilation of available emission factors for sources of organic compounds (including hydrocarbons) operated without control equipment, except where noted. Emission factors were compiled from a recent U.S. Public Health Service Publication.[27]

Data on emission factors for the process industries do not include values for surface coating or degreasing operations. The solvents and thinners used in these operations all evaporate to the atmosphere unless controlled. A somewhat similar situation exists in the case of paint varnish and resins manufacturing. Remember that the emission factors listed are average values and can vary depending upon operating conditions as well as upon specific equipment factors. There are, of course, many process sources of hydrocarbon emissions other than those listed in Table 2-9.

Examples of the use of emission factors are given below:

I. Coal combustion

Given: Power plant burns 100,000 tons per year of coal

$$(100{,}000\ \text{tons/year})\ \left(0.2\ \frac{\text{lb of HC}}{\text{ton of coal}}\right) = 20{,}000\ \text{lb of HC/year}$$

II. Gasoline-powered vehicle

Given: 1960 uncontrolled automobile using 1,000 gallons a year of gasoline

$$\text{Exhaust emissions:}\ \left(1000\ \frac{\text{gallons}}{\text{year}}\right)\ \left(208\ \frac{\text{lb}}{1000\ \text{gal}}\right)\ \text{of HC/year}$$

Table 2-9. HYDROCARBON EMISSION FACTORS.

Source	Lb. of Hydrocarbons and/or Organics Per Unit Given	Unit
FUEL COMBUSTION - STATIONARY SOURCES (AS METHANE)		
Coal		
10×10^6 BTU/hr capacity	10	ton of coal burned
10 to 100×10^6 BTU/hr capacity	1	ton of coal burned
Greater than 100×10^6 BTU/hr capacity	0.205	ton of coal burned
Fuel Oil		
10×10^6 BTU/hr capacity	5	1,000 gallons of oil burned
10 to 100×10^6 BTU/hr capacity	4	1,000 gallons of oil burned
Greater than 100×10^6 BTU/hr capacity	3.8	1,000 gallons of oil burned
Natural Gas	Negligible	
Wood[30]		
FUEL COMBUSTION - MOBILE SOURCES		
Gasoline-powered motor vehicle (as carbon)		
Exhaust[a,b] [27,32]	208-404	1,000 gallons of gas burned
	or 13.1 - 25.4	1,000 vehicle miles
Crankcase[c] [32]	128	1,000 gallons of gas burned
Evaporative (carburetor and fuel tank)[d]	92	1,000 gallons of gas throughput
Diesel-powered vehicle [27,32] (as carbon)	177-221	1,000 gallons of diesel fuel

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[a] Based on an average route speed of 25 miles per hour. Emission factors for various speeds can be found in Reference 27.

[b] 1968 exhaust control devices were expected to reduce exhaust hydrocarbons by 70 percent and 1970 devices should reduce exhaust hydrocarbons by 80 percent.

[c] 1963 blowby devices reduced crackcase hydrocarbon emissions approximately 80 percent while 1968 devices were expected to control these emissions 100 percent.

[d] Anticipated control of 90 percent by 1971.

Table 2-9 (cont'd)

Source	Lb. of Hydrocarbons and/or Organics Per Unit Given	Unit
Aircraft (as methane)		
Jet[31] (conventional)		
4 engine	7.24	Flight[e]
3 engine	5.43	Flight
2 engine	3.62	Flight
1 engine	1.81	Flight
Jet[31] (fan-type)		
4 engine	31.2	Flight
3 engine	23.4	Flight
2 engine	15.6	Flight
1 engine	7.8	Flight
Turbo-prop[31]		
4 engine	2.47	Flight
2 engine	1.24	Flight
Piston		
4 engine	60.5	Flight
2 engine	25.2	Flight
SOLID WASTE DISPOSAL		
Open burning on-site of leaves, brush, paper, etc.[27,30]	12-415	ton of waste burned
Open burning dump[30]	80	ton of waste burned
Municipal incinerator[27,30]	1.2-3.1	ton of waste burned
Multiple chamber incinerator	3.7	ton of waste burned
Single chamber incincerator[27,32]	4.8-114	ton of waste burned
Flue fed incinerator[27,32]	30-67	ton of waste burned
Domestic incinerator[27,32]	14.5-119	ton of waste burned

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[e] Flight is defined as a combination of landing and take-off.

Table 2-9 (cont'd)

Source	Lb. of Hydrocarbons and/or Organics Per Unit Given	Unit
Petroleum refinery (as total hydrocarbons)		
Boilers and process heaters	165	1,000 bbl. oil burned
Fluid catalytic unit	239	1,000 bbl. fresh feed
Moving-bed catalytic cracking unit	99	1,000 bbl. fresh feed
Compressor internal combustion engines	1.31	1,000 ft.^{3} of fuel gas burned
Blowdown system		
with control	5	1,000 bbl. refinery capacity
without control	300	1,000 bbl. refinery capacity
Process drains		
with control	8	1,000 bbl. waste water
without control	210	1,000 bbl. waste water
Vacuum jets		
with control	Negligible	1,000 bbl. vacuum distillation capacity
without control	130	1,000 bbl. vacuum distillation capacity
Cooling towers	6	10^6 gallon cooling water capaci

Table 2-9 (Cont'd)

Source	Lb. of Hydrocarbons and/or Organics Per Unit Given	Unit
Pipeline valves and flanges	28	1,000 bbl. refinery capacity
Vessel relief valves	11	1,000 bbl. refinery capacity
Pump seals	17	1,000 bbl. refinery capacity
Compressor seals	5	1,000 bbl. refinery capacity
Air blowing, blend changing, and sampling	10	1,000 bbl. refinery capacity
Storage		
V.P.$\geq$1.5 psia-fixed roof	47	1,000 bbl. storage capacity
V.P.$\geq$1.5 psia-floating roof	4.8	1,000 bbl. storage capacity
V.P.$\leq$1.5 psia-fixed roof	1.6	1,000 bbl. storage capacity
Dry cleaning		
Chlor-hydrocarbons	1.7	capita-year
Hydrocarbon vapors	2.2	capita-year
Gasoline handling (evaporation)		
Filling tank vehicles		
Splash fill	8.2	1,000 gallons throughput
Submerge fill	4.9	1,000 gallons throughput
Filling service station tanks		
Splash fill	11.5	1,000 gallons throughput
Submerge fill	7.3	1,000 gallons throughput
Filling automobile tanks	11.6	1,000 gallons throughput

Crankcase emissions: $(1000\ \frac{\text{gallons}}{\text{year}})\ (128\ \frac{\text{lb}}{1000\ \text{gal.}}) =$

128 lb of HC/year

Evaporative losses: $(1000\ \frac{\text{gallons}}{\text{year}})\ (92\ \frac{\text{lb}}{1000\ \text{gal.}}) =$

92 lb of HC/year

Total Automobile Emissions = $428\ \frac{\text{lb of HC}}{\text{year}}$

b. Nitrogen Oxides Emissions

1) Types of Sources

As previously stated, the major source of nitrogen oxides results from the high temperature reaction between nitrogen and oxygen in air used for combustion with various fuels. On a nationwide basis, the quantities of NO_x produced in this manner are estimated to be as high as 98 percent of the total technological nitrogen oxides emissions.

Thus the production of NO_x can be viewed as a by-product or side reaction proceeding initially as follows:

$$N_2 + O_2 = 2NO$$

The nitric oxide (NO) formed may be further oxidized to nitrogen dioxide (NO_2), although more than 90 percent of the nitrogen oxides formed in combustion operations are in the form of nitric oxide. Other sections of this report deal with the various atmospheric reactions which may take place subsequent to discharge.

Many factors influence the actual amount of nitrogen oxides formation, including flame temperature, fuel-to-air ratio, mixing, residence time, and pressure. In general very large, efficient, high temperature combustion units such as those used to produce steam for electric power generation produce the highest concentrations of nitrogen oxides. Much smaller quantities, proportionately, are produced by small units such as household water heaters.

A wide variety of combustion operations are found in almost every facet of our business and everyday life. The largest single category here would be the fossil-fueled (coal, oil, and gas) steam electric-generating plants. Other significant categories include commercial and domestic space heaters, stationary engines, process heaters, and incinerators.

A slightly different category of combustion operation includes industrial furnaces and ovens. These are used for smelting metal ores, refining metal, manufacturing cement and glass, producing refractives, processing other minerals, and baking and drying protective and decorative surface coatings.

Nitrogen oxide emissions from noncombustion industrial processes are almost entirely limited to the manufacturing and use of nitric acid. The principal uses of nitric acid are ammonium nitrate production, oxidation of organic intermediates, nitration processes such as explosives production, acidulation of phosphate rock for fertilizer production, and metal surface treating. The nitrogen oxides emitted from these processes result principally from the reduction or decomposition of nitric acid. Both nitrogen dioxide and nitric oxide are found. Even though total quantities may be small, high concentrations of nitrogen oxides may be produced in certain of these chemical processes.

2) Emission Factors

The development of emission factors for nitrogen oxides has been a complex and difficult problem. For combustion sources alone a whole set of interacting factors such as equipment size, burner type, cooling surface area, firing rate, type of fuel, and air/fuel ratio are involved. While predictive formulae and nomograms have been developed for nitrogen oxides emissions from a variety of combustion sources,[33] a wide range of values has been obtained from seemingly similar sources.

Similar problems exist in the development of factors for noncombustion sources. Most such processes utilize some built-in control equipment for economic reasons alone, making a simple distinction between uncontrolled and controlled factors nearly impossible. Many other variables such as raw material composition and production rate also have a significant influence on the emission factors for any given situation. Nevertheless, Table 2-10 presents estimates of emission factors for nitrogen oxides.[27]

E. PRINCIPLES OF HYDROCARBON AND NITROGEN OXIDES CONTROL

1. Hydrocarbons

The control of hydrocarbon vapors from technological sources rests upon several basic principles. These include (1) restriction of evaporative loss, (2) recovery by mass transfer principles, (3) optimization of combustion processes, and (4) substitution of process materials and fuels for those having altered chemical or physical properties.

Table 2-10. NO_x EMISSION FACTORS[27].

Fuel	Household and Commercial	Industry	Electric Generation	Transportation
1. Natural gas	116 lb/10^6 ft^3 (58 tons/10^9 ft^3)	214 lb/10^6 ft^3 (107 tons/10^9 ft^3)	390 lb/10^6 ft^3 (195 tons/10^9 ft^3)	
2. Coal	8 lb/ton (4 tons/1000 tons)	20 lb/ton (10 tons/1000 tons)	20 lb/ton (10 tons/1000 tons)	
3. Jet Fuel	--	--	--	23 lb/Flight Conv 9.2 lb/Flight Fan-jet
4. Gasoline	--	--	--	113 lbs/1000 gals (2373 tons/10^6 BBL)
5. Kerosene, Distillate and Residual Fuel Oil	12-72 lb/1000 gal (252-1512 tons/10^6 BBL)	72 lb/1000 gal (1512 tons/10^6 BBL)	104 lb/1000 gal (2184 tons/10^6 BBL)	222 lbs/1000 gals (4662 tons/10^6 BBL)

NO_x Emission Factors (Pounds NO_x/10^9 BTU)

Fuel	Household and Commercial	Industry	Electric Generation
1. Natural Gas (1046 BTU/cu ft)	111	205	373
2. Coal (11,867 BTU/pound)	337	842	842
3. Fuel Oil (149,966 BTU/ gal)	80-480*	480	680

*80 for household-size units, 480 for average commercial size.

The applications of these principles depend upon whether the emissions arise from product storage and transfer, industrial processes, or combustion. Vehicular sources involve a complex mix of both evaporative and combustion losses.

a. Present Motor Vehicle Controls

1) Blowby Gases

During the compression, power and exhaust strokes of a 4-cycle internal combustion gasoline engine, gases present in the cylinder space above the piston are at pressures above that of the atmosphere. Because the piston rings do not constitute a perfect seal, a portion of the gas mixture is forced by the rings into the crankcase during each of the above-mentioned conditions. These so-called "blowby" gases contain varying amounts of unburned or partially burned hydrocarbons. Of the total hydrocarbon emissions from uncontrolled vehicles, approximately 20 percent originate from blowby.

Essentially 100 percent control of blowby hydrocarbon is achieved by closing the normal crankcase vents and returning the gases through appropriate piping to the intake manifold. In essence, these gases are recycled through the combustion process. To avoid rough idling, flow is regulated by a spring-loaded valve in the return line.

The successful application of this technique has required the use of higher detergent gasolines and lubricating oils to minimize carburetor deposits and sludge formation in oil.

2) Exhaust Gas

The reduction of hydrocarbons in exhaust gases is accomplished by one of two general approaches in systems presently in use.

The first principle involves the injection of controlled amounts of additional combustion air at the cylinder exhaust ports. This further oxidizes the unburned or partially burned hydrocarbons in the oxygen-deficient exhaust gases. The introduction of this additional air requires an auxiliary compressor. With the increasing use of the engine modification approach to control, the application of the air injection technique has become concentrated in automobiles having manual transmissions.

The second and most widely used approach to exhaust gas hydrocarbon control is preventive in nature. It involves a series of integrated engine and engine-accessory modifications designed to improve overall combustion efficiency (not to be confused with energy-utilization efficiency). Major elements involved in the engine modification approach include:

1. Leaner air-to-fuel ratios.
2. Improved air-fuel mixing.
3. More uniform air-fuel mixture distribution.
4. More precise fuel metering.
5. Improved cylinder combustion conditions.

Attainment of these design objectives has been accomplished by a number of measures, not all of which are used in any one system. Measures which have been used include leaner idle and cruise fuel-metering settings, combustion-air temperature control, dual intake manifolds, fuel injection, spark retardation combined with more open throttle during idle, and combustion chamber redesign to minimize extent of quench zones (areas where premature combustion termination occurs).

3) Evaporation

Approximately 10 percent of the total hydrocarbon emission from an uncontrolled automobile is from evaporation of fuel from the fuel tank and carburetor.[21] Most fuel tank losses occur during filling, when air saturated with gasoline vapor is displaced by the liquid gasoline; however, losses also result from heat expansion of the air space over the fuel during the normal daytime heating cycle. As the vapor pressure of gasoline rises with increased temperatures, this type of evaporative loss is accentuated on very warm days following cool nights.

Carburetor losses occur following engine shutdown, when the more volatile fraction of the fuel in the carburetor evaporates. This is termed the "hot soak" loss, as a substantial amount of heat is transferred from the hot engine to the carburetor body during this period.

Evaporation controls, effective in California for 1970 automobiles and in 1971 nationally, consist of a means for conducting the fuel vapors to either the crankcase or an activated charcoal canister. In the first case the vapors are merely held in the air space, while the charcoal actually absorbs them. The gasoline thus collected is eventually returned to the induction system for burning in the engine at a time when engine performance will not be affected.

b. Proposed Motor Vehicle Controls

More restrictive motor vehicle emission controls for hydrocarbons will require the application of control techniques beyond those now in use. First steps might include direct and catalytic exhaust manifold reactors, more drastic engine modification, and fuel alteration. The latter approach envisions reduction in volatility and substitution of less reactive hydrocarbons for certain of the components (principally olefins) now commonly present. This type of hydrocarbon control is most effective on evaporative losses and becomes less meaningful where mechanical evaporative controls are used.

Beyond the hydrocarbon control now thought possible with the present 4-cycle, spark-ignited, gasoline-fueled, internal combustion engine, other types of motive power have been advanced and publicized. These have sometimes been described as "low emission" systems and include the gas turbine, electric drive, the steam engine, the Stirling engine, and the stratified charge engine. Other suggestions involve the complete substitution of liquified petroleum gases--or, as a special case, liquefied natural gas--for gasoline as a fuel.

Proposals for reduction of hydrocarbon emissions from vehicular sources extend to areas other than the use of specific vehicular emission standards. These include:

1. Substitution, in part, of public transportation for private motor vehicles.

2. Improved road design and traffic control systems so as to reduce high-emission, stop-and-go driving.
3. Restriction by regulation or by economic incentive of the use of private vehicles.

These areas fall within the jurisdiction of the individual states, and will require major evaluation efforts.

c. Stationary Source Controls

Control principles used for stationary sources of hydrocarbons and related organic substances include (1) evaporation prevention (including vapor recovery), (2) incineration, (3) adsorption, (4) absorption, (5) condensation, and (6) substitution of less volatile and less photochemically reactive materials in solvents for cleaning and surface coating use. A brief description follows of the principles involved for each.

1) Evaporation

As a general principle, the direct control of hydrocarbon evaporation involves the minimization of liquid-air contact. Major opportunities for such control are in the storage and transfer of materials, e.g., gasoline. One approach involves the substitution of floating roofs for fixed roofs in storage tanks. This eliminates the air space between the surface of the liquid and the tank roof, thus reducing the loss of vapors during tank fueling operations and during the daily contraction and expansion of air resulting from day and night temperature differences.

Vapor recovery systems physically move excess vapors to a control unit such as a compressor-condensor system. They are normally used only with hydrocarbons of rather high vapor pressure.

2) Incineration

Incineration acts by combustion of hydrocarbon or other organic emissions. Product recovery is thus eliminated, but by-product heat may sometimes be utilized. Incineration is only used where the products of combustion are innocuous.

A successful combustion control process requires adequate heat impact, good mixing and sufficient residence time to result in complete combustion. Less than optimum conditions may result in partial oxidation only.

3) Adsorption

Adsorption is a physical process whereby gas molecules are attracted to and held on solid surfaces. Certain solids such as activated alumina, silica gel, and activated carbon have these properties to the extent that they have practical applications. Further, these materials are prepared so that they have a very large surface-to-volume ratio.

Adsorbents are generally selective in their properties, the most distinguishing feature being their relative polarity. Polar adsorbents preferentially adsorb water, while nonpolar solvents select organic substances. For this reason activated carbon, a nonpolar adsorbent, is most commonly used for control of organic emissions.

4) Absorption

Absorption is the process by which gases or vapors are collected in a relatively nonvolatile liquid absorbent. To be effective, the absorbent should have the capability of holding relatively large quantities of the solute gas at normal temperatures.

Absorbents tend to have the greatest holding capacities for related classes of materials. Thus organic absorbing liquids would normally be used for collection of hydrocarbon and other organic vapors. The relatively low capacities of organic absorbents have minimized the utility of this approach to hydrocarbon control.

5) Condensation

Condensation normally involves the reduction of temperature of a vapor-air mixture to a point below which the concentration of the vapor exceeds the saturation vapor pressure. The technique is most suitable for higher vapor concentrations as substantial quantities of vapor may coexist with the liquid phase even at the colder temperatures practically obtainable. Condensation for air pollution control is generally used as a pretreatment to reduce the load on a more efficient process, such as adsorption or incineration.

6) Substitution of Materials

The substitution of photochemically nonreactive materials as a stationary source control measure has been largely limited to the use of solvents in degreasing operations, surface coatings and printing inks. A prime example exists in architectural surface coatings, where the evaporating solvent cannot be confined for disposal. Use of the approach in cleaning solvents and in industrial surface coatings is largely dependent upon technological and economic parameters. In some cases satisfactory reformulation of products with nonreactive solvents has been difficult, and in some cases the increased costs are greater than those for control equipment.

2. Nitrogen Oxides

The control of nitrogen oxides from technological sources is at present very much in a developmental stage. For those sources involving the production of such emissions as a by-product of high temperature combustion, major effort is being devoted to process and design modifications which will result in minimizing the formation of nitric oxide. Fundamentally, this means avoidance of peak temperatures and pressures. Some effort is directed towards evaluation of stack gas removal, although even greater developmental problems are expected here.

Emission control of nitrogen oxides from chemical processes may be viewed from either the process alteration or vent gas removal approach.

a. Proposed Motor Vehicle Controls

At present, control of nitrogen oxides from motor vehicles has reached only the laboratory or demonstration phase. Consequently, all control approaches must be viewed as potential. Essentially, all the nitrogen oxides emissions from motor vehicles are in the exhaust gases resulting from the fixation of nitrogen with air in the engine during combustion of fuel and air. This is true for gas turbine engines as well as conventional gasoline piston and diesel engines.

Major control efforts to date have been based upon attempts to reduce the formation of nitrogen oxides rather than control them in the exhaust, although the latter approach has certainly not been rejected. Because nitrogen oxides production is enhanced by high flame temperatures and relative oxygen concentrations, most control approaches involve either flame temperature reduction, air/fuel ratio alteration, or some combination of both. In most cases, the two factors interact.

Specific control approaches now being considered all suffer some potential drawbacks: They may alter engine performance from the standpoint of drivability or economy; they may add considerably to the complexity or expense of the engine, e.g., fuel availability, vehicle range; finally, they may complicate the control of hydrocarbons and carbon monoxide.

Most development activity now underway utilizes one of the following approaches:

1) Inert Gas Dilution

Recirculated exhaust gas or even water injection can be used as a heat sink during combustion and thus reduce flame temperature. Some power is sacrificed and engine operations may be rough unless the charge is very well homogenized.

2) Air/Fuel Ratio Adjustment

Enrichment or leaning, i.e., excess fuel in the former and excess air in the latter, will reduce nitrogen oxides formation by changing the oxygen content away from that amount optimum for maximum NO_x production. Fuel enrichment would require additional measures to control hydrocarbon and carbon monoxide. Excess air is limited by engine stalling.

3) Combustion Alteration

A variety of techniques can be classified here, including ignition timing, injection timing (in injected engines), use of precombustion chambers, stratified charging, and better homogenization. All are designed to reduce peak flame temperatures.

4) Fuel Alteration

Liquefied natural gas, liquefied petroleum gases (propane and butane) and nongasoline fuels have all been considered as an approach to nitrogen oxides control. In some cases they can be burned with higher quantities of excess air or they may have lower heat content as compared to gasoline. In either case, reduced flame temperatures result.

5) Catalytic Reactors

Exhaust gas treatment with either reduced or mixed oxidation/reduction catalysts are under consideration as an alternative to engine modifications. These act to reduce the nitric oxide in the exhaust to nitrogen. Major practice problems such as catalyst life have been encountered.

The above list should not be considered complete. a summary of the most general approaches to control of nitrogen oxides, many combinations of which are under consideration. More drastic "low emission" approaches are discussed briefly under hydrocarbon controls.

b. Stationary Source Controls

Control of nitrogen oxides from stationary sources, as in the case of motor vehicle controls, may be covered under the broad categories of combustion alteration or stack gas removal. However, there is generally more latitude available for consideration of the various alternatives in at least some of the stationary sources.

In the case of large combustion units the major design objective is to reduce peak temperatures. Techniques under consideration or trial include altered burner design, change in burner placement, stage combustion, exhaust gas recirculation, steam or water injection, and control of excess air. Although details obviously differ, there is a great deal of inherent similarity here as compared to motor vehicle controls; consequently, little additional space is given to examining these control methods. The major consideration is to obtain the maximum nitrogen oxides reduction consistent with safety and fuel economy.

Somewhat greater consideration has been given to nitrogen oxides removal from stationary source stack gases than from the motor vehicle. For combustion sources some of the specific processes which are being considered include:

1) Reinluft Char Process

Activated char is used to remove primarily sulfur dioxide, but will also remove some NO by oxidation and subsequent adsorption.

2) Tyco Modified Lead Chamber Process

The chemistry of the lead chamber process is used in which concentrated sulfuric acid removes both sulfur and nitrogen oxides.

3) Atomics International Molten Carbonate Process

Molten carbonate salts are used to absorb oxides of sulfur and nitrogen. The latter are removed at about 20 to 30 percent of the efficiency for sulfur dioxide.

4) Limestone Scrubbing Process

Pilot studies indicate that 20 percent of the nitric oxide present in the stack gases is removed in the wet limestone (or other alkali) scrubbing process designed for sulfur dioxide removal.

Other stack gas removal techniques are used for nitrogen oxides in the tail gases of chemical plants using nitric acid. Final cleanup techniques are usually designed to catalytically reduce the nitrogen oxides to nitrogen. Effluent streams are usually lower in volume and higher in NO_x concentration in chemical plants as compared to large combustion processes, thus making the design process somewhat simpler.

F. NATURE OF PHOTOCHEMICAL REACTANTS

1. Hydrocarbon Classes and Properties

Hydrocarbons are compounds whose molecules contain atoms of hydrogen and carbon only. All compounds of carbon, except the oxides of carbon and the carbonates, are organic compounds. This class, therefore, includes the hydrocarbons as well as many other carbon compounds having additional elements such as oxygen, nitrogen, and chlorine.

The hydrocarbons of interest in this document are those which may be encountered in the gas phase in urban atmosphere, especially those emitted into the atmosphere as contaminants by air pollution sources. Regardless of their further classification, which is discussed below, the volatility of hydrocarbons is approximately determined by their carbon number. Those having carbon numbers of 1 to 4 are gaseous at ordinary temperatures, while those with carbon numbers of 5 or more are liquids or solids in the pure state. (Liquid mixtures of hydrocarbons, such as gasoline, may include some proportion of compounds which in the pure state would be either gases or solids.) Hydrocarbons having a carbon number (i.e., number of carbon atoms in each molecule) greater than 12 are generally not sufficiently volatile to reach troublesome concentrations in the atmosphere in the gas phase; however, many of these higher hydrocarbons, as particles or associated with particulate matter, are important air contaminants in another context.

Hydrocarbons fall into three main classes which are defined in terms of their general molecular structure: aliphatic, aromatic, and alicyclic. Aliphatic hydrocarbons are all those whose carbon atoms are arranged in chains only--with or without branching chains, but without rings. Aromatic hydrocarbons are all those whose carbon skeletons include benzene rings, i.e., six-membered carbon rings with only one additional atom (of hydrogen or carbon) attached to each atom in the ring. A subsidiary classification often used is that of saturated vs. unsaturated. A saturated hydrocarbon is one with each of its carbon atoms bonded to four other atoms, generally carbon or hydrogen; an unsaturated hydrocarbon is one with one or more carbon atoms bonded to less than four other atoms. Saturated aliphatic hydrocarbons all correspond to the empirical formula C_nH_{2n+2}, where n is the carbon number. Saturated alicyclics with one ring have the formula C_nH_{2n}; those with two rings have the formula C_nH_{2n-2}, and so on. All aromatic hydrocarbons are unsaturated.

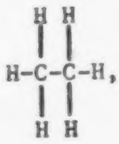
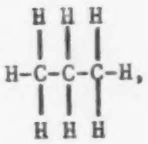
The classes of hydrocarbons, their properties in general, and particular compounds of importance are discussed in the remainder of this section.

a. Aliphatic Hydrocarbons

Subclassification of aliphatic hydrocarbons is based principally upon the extent and type of unsaturation evident in their molecular structure. In the modern, systematic nomenclature, saturated aliphatics are known as alkanes; unsaturated aliphatics with no triple bonds are alkenes; and those with triple bonds (characterized by pairs of adjacent carbon atoms each connected to only one other atom) are alkynes. In structural formulae, the double bond is represented by two lines between a pair of adjacent carbon atoms, e.g., C=C, and the triple bond by three lines, e.g., C≡C.

In older but still widely used terminology, alkanes are paraffins, alkenes are olefins and alkynes are acetylenes. The corresponding terms are synonymous and are so used in the chemical profession. A systematic procedure for naming organic compounds has been developed by the International Union of Pure and Applied Chemistry (IUPAC). A comprehensive treatment of these rules can be found in various treatises and texts in organic chemistry; in this section, common names of the better known compounds are given, as well as IUPAC names and any frequently used alternatives.

1) Alkanes (Paraffins)

Generally, alkanes are relatively stable and unreactive hydrocarbons whose chemical reactions depend upon breaking carbon-hydrogen bonds. Such differences in reactivity as exist between them depend on the number of hydrogen atoms occupying certain positions relative to the carbon skeleton of the molecule, which in turn depends on the degree of branching of the carbon skeleton. Hydrogen atoms in hydrocarbon molecules are classed as primary, secondary or tertiary according to whether the carbon atoms to which they are bonded are also bonded to one, two or three other carbon atoms. Thus in ethane,  $H-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-H$, there are six primary hydrogen atoms, while in propane,  $H-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-H$, there are six primary and two secondary hydrogen atoms.

In the straight-chain paraffins ("normal" alkanes or n-alkanes), all hydrogen atoms are primary or secondary. The least reactive are the lowest two members of the class, methane and ethane, in which all hydrogen atoms are primary. Branched paraffins, also called isoparaffins, isoalkanes, or i-alkanes, often have tertiary hydrogen atoms, which confer somewhat higher reactivity.

a) n-Alkanes

Table 2-11 lists names, formulae and boiling points of the n-alkanes by carbon number through 10. The lowest members of the series, methane, ethane and propane, are the main constituents of natural gas, of which methane usually constitutes 90 percent or more (by volume). The higher boiling paraffin gases, propane and butane, are important constituents of liquid petroleum gas (LPG), and the paraffins of carbon number 5 and over are constituents of gasoline.

b) i-Alkanes

Table 2-12 presents carbon skeletons, names and boiling points of all the isoalkanes of carbon numbers 4, 5 and 6. With higher carbon numbers there are larger numbers of isomers: 7 for carbon number 7, 15 for carbon number 8, etc. Consequently, many such compounds exist in the boiling range of gasoline.

2) Alkenes (Olefins)

The alkenes are generally somewhat more reactive than most alkanes because substituent atoms can be added to their structures without the necessity of rupturing carbon-hydrogen bonds. Due to the wide variety of individual modes of action with different reagents, further generalizations regarding reactivity are not warranted. Table 2-13 presents carbon skeletons, names, and boiling points of all the monoalkenes of carbon numbers up to 5; there are larger numbers of isomers for higher carbon numbers. For example,

Table 2-11. PROPERTIES OF SOME n-ALKANES.

Carbon Number	Name	Formula	Boiling Point, °C
1	Methane	CH_4	-161.7
2	Ethane	C_2H_6	- 88.6
3	Propane	C_3H_8	- 42.2
4	Butane	C_4H_{10}	- 0.5
5	Pentane	C_5H_{12}	36.1
6	Hexane	C_6H_{14}	68.7
7	Heptane	C_7H_{16}	98.4
8	Octane	C_8H_{18}	125.6
9	Nonane	C_9H_{20}	150.7
10	Decane	$C_{10}H_{22}$	174.0

Table 2-12. PROPERTIES OF SOME ISOALKANES.

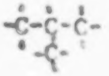
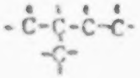
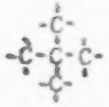
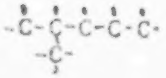
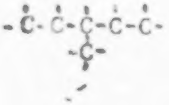
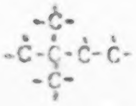
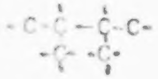
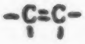
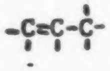
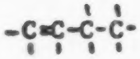
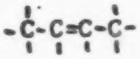
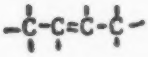
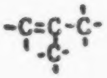
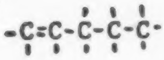
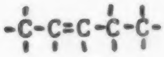
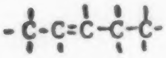
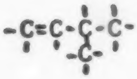
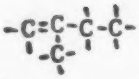
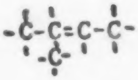
Carbon Number	Carbon Skeleton	Name	Boiling Point,°C
4		Isobutane (2-methylpropane)	-10
5		Isopentane (2-methylbutane)	28
		Neopentane (2,2-dimethylpropane)	10
6		2-Methylpentane	60
		3-Methylpentane	64
		2,2-Dimethylbutane	50
		2,3-Dimethylbutane	58

Table 2-13. PROPERTIES OF SOME ALKENES (OLEFINS).

Carbon Number	**Carbon Skeleton**	**Name**	**Boiling Point, °C**
2	 $-C=C-$	Ethylene (Ethene)	-102
3	 $-C=C-C-$	Propylene (Propene)	-48
4	 $-C=C-C-C-$	1-Butene	-6
	 $-C-C=C-C-$	*cis*-2-Butene	-4
	 $-C-C=C-C-$	*trans*-2-Butene	-3
	 $-C=\underset{-C-}{C}-C-$	Isobutene (2-Methylpropene)	-7
5	 $-C=C-C-C-C-$	1-Pentene	30
	 $-C-C=C-C-C-$	*cis*-2-Pentene	36
	 $-C-C=C-C-C-$	*trans*-2-Pentene	
	 $-C=C-\underset{-C-}{C}-C-$	3-Methyl-1-butene	25
	 $-C=\underset{-C-}{C}-C-C-$	2-Methyl-1-butene	31
	 $-C-\underset{-C-}{C}=C-C-$	2-Methyl-2-butene (Trimethylethylene)	38

there are 14 isomers of carbon number 6, including pairs of optical isomers. It should be noted that 2,3-dimethyl-2-butene is commonly called tetramethylethylene.

Ethylene is the most abundant olefin in auto exhausts, and therefore is presumably the most abundant in urban atmospheres. Of all the aliphatic hydrocarbons, it is the only one known to produce any biological action at concentrations thus far observed in urban atmospheres; this is a phytotoxic effect, especially damaging to some flowers.

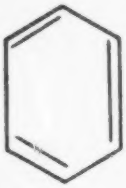
Alkenes having two double bonds in the molecule are also known; the simplest are propadiene or allene, C_3H_4: $(-\underset{|}{C}=C=\underset{|}{C}-)$; 1,2-butadiene or methallene, $(-\underset{|}{C}=C=\underset{|}{C}-\underset{|}{C}-)$; and 1,3-butadiene $(-\underset{|}{C}=\underset{|}{C}-\underset{|}{C}=\underset{|}{C}-)$. The last is of particular interest because it may be a precursor of acrolein, a particularly potent eye irritant in photochemical smog.

3) Alkynes (Acetylenes)

Alkynes contain one or more triple bonds (in addition to any double bonds) in the molecule. The first member of the series is acetylene or ethyne, C_2H_2 ($H-C\equiv C-H$); the next, methylacetylene or propyne ($H-C\equiv C-CH_3$). These two compounds are found in auto exhaust, but are relatively inert in photochemical reactions.

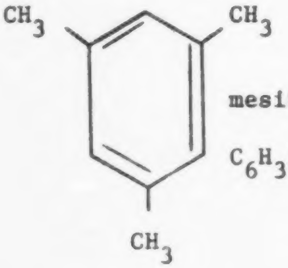
b. Aromatic Hydrocarbons

Aromatic hydrocarbons comprise benzene and many compounds with structures related to that of benzene. The structure of benzene, C_6H_6, is that of a simple, symmetrical ring of six carbon atoms, to each of which a hydrogen atom is attached. For convenience, the benzene structure is usually represented by a hexagon with three double bonds, without any representation of the carbon or hydrogen atoms. Thus:



benzene, C_6H_6

Other aromatic hydrocarbons are shown with substituent groups attached to the ring, with the implication that each substituent group has replaced one hydrogen atom. Thus:

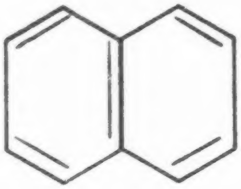


mesitylene or 1,3,5-trimethylbenzene, $C_6H_3(CH_3)_3$

The prefixes *o*-, *m*-, and *p* (for ortho, meta, and para) are used to describe the relative positions of substituents on the ring when there are two substituents. Thus, there are three dimethylbenzenes, commonly known as xylenes; in *o*-xylene, the substituent methyl groups occupy adjacent ring positions; in *m*-xylene they are separated by one ring position, and in *p*-xylene they are separated by two. When there are more than two substituents, they are designated by numbering the ring positions.

Table 2-14 shows names, structural formulae and boiling points of some of the lower aromatics. All the aromatics of carbon numbers 6, 7 and 8 are included, but not all of carbon number 9. Although the aromatic hydrocarbons are unsaturated, their ring structures are less susceptible to addition of substituents than are the double bonds of alkenes. Benzene itself is practically inert to reactions in the photochemical smog complex. Where the side-chain substituents contain double bonds, as in styrene, addition reactions are likely to involve these double bonds and to leave the ring structure intact.

Many aromatic compounds have more than one benzene ring, or "fused" ring structures, of which naphthalene is an example:



$C_{10}H_8$, naphthalene.

However, all these compounds have carbon numbers of 10 or more. They are therefore not very volatile, not abundant in gasoline or auto exhaust, and of little importance in photochemical smog.

c. Alicyclic Hydrocarbons (Naphthenes)

Alicyclic hydrocarbons are divided into the cycloalkanes, the cycloalkenes and the cycloalkynes, sometimes called cycloparaffins, cycloolefins, and cycloacetylenes, respectively. These classes are analogous to the classes of aliphatic hydrocarbons discussed above, being based on the degree and type of unsaturation in the molecule. Their reactivity is for the

Table 2-14. PROPERTIES OF SOME AROMATIC HYDROCARBONS.

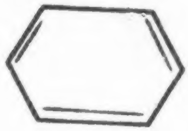
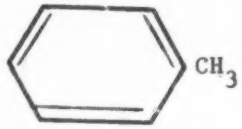
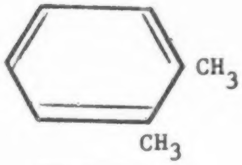
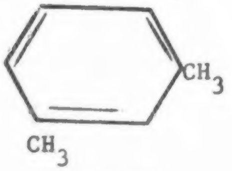
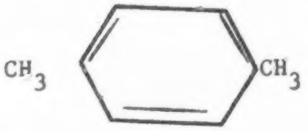
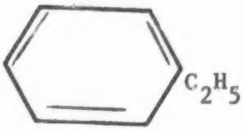
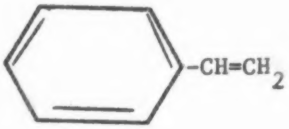
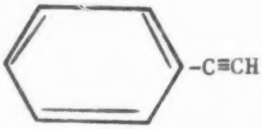
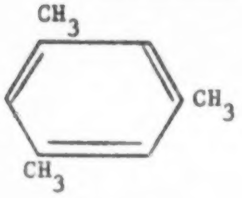
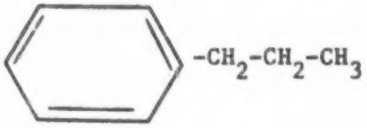
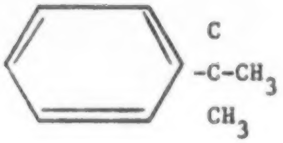
Carbon Number	Structure	Name	Boiling Point, °C
6		**Benzene**	80
7		Toluene (Methylbenzene)	111
8		*o*-Xylene (1,2-Dimethylbenzene)	144.0
		*m*-Xylene (1,3-Dimethylbenzene)	139.3
		*p*-Xylene (1,4-Dimethylbenzene)	138.5
		Ethylbenzene	136
		Styrene (Vinylbenzene)	146
		Phenylacetylene (Ethynylbenzene)	

Table 2-14. (Cont'd)

Carbon Number	Structure	Name	Boiling Point, °C
9		Mesitylene (1,3,5 Trimethylbenzene)	165
		n-Propylbenzene	160
		Cumene (Isopropylbenzene)	152

most part similar to that of corresponding aliphatics of the same carbon number and degree of unsaturation. However, some of the alicyclics, with three- or four-membered rings, are appreciably less resistant to certain reagents than are the corresponding aliphatics. Names of the basic ring structures are also analogous to those of the corresponding aliphatics. Names and boiling points of some of the unsubstituted cycloalkanes are presented in Table 2-15. Cyclopentane, cyclohexane and some of their alkyl derivatives, such as methylcyclopentane, are present in appreciable proportions in gasoline and automobile exhaust.

2. Hydrocarbons in Ambient Air

Table 2-16 lists the individual hydrocarbons detected in samples of urban air by gas chromatographic analysis in several investigations.[8,34,35] A total of 56 compounds have been thus detected, of which 17 were alkanes, 23 alkenes (including two alkadienes), 2 alkynes, 10 aromatics, 3 cycloalkanes and 1 cycloalkene. It is certain that the length of this list is limited only by the sensitivity of the analytical methods, and that many additional hydrocarbon compounds are actually present in urban air, although in lower concentrations than those listed. Especially at the higher carbon numbers, the complexity of the chromatographic records becomes so great that the effort to interpret them in terms of individual compounds may be insufficiently rewarding. For this reason the list in the table must be considered as severely truncated for carbon numbers of 7 and higher.

Table 2- 15. PROPERTIES OF SOME CYCLOALKANES.

Carbon Number	Name	Formula	Boiling Point, °C
3	Cyclopropane	C_3H_6	-33
4	Cyclobutane	C_4H_8	12
5	Cyclopentane	C_5H_{10}	49
6	Cyclohexane	C_6H_{12}	81
7	Cycloheptane	C_7H_{14}	117
8	Cyclooctane	C_8H_{16}	147

Table 2-16. SOME HYDROCARBONS IDENTIFIED IN AMBIENT AIR.

Carbon Number	Class	Compound	References
1	Alkane	Methane	a
2	Alkane	Ethane	a,c
	Alkene	Ethylene	a,c
	Alkyne	Acetylene	a,c
3	Alkane	Propane	a,c
	Alkene	Propylene	a,b,c
		Propadiene	a
	Alkyne	Methylacetylene	a
4	Alkane	Butane	a,c
		Isobutane	a,c
	Alkene	1-Butene	a,c
		cis-2-Butene	a,b,c
		trans-2-Butene	a,b,c
		Isobutene	a,b,c
		1,3-Butadiene	a,b,c
5	Alkane	Pentane	a,b,c
		Isopentane	a,b,c
	Alkene	1-Pentene	a,b,c
		cis-2-Pentene	a,b,c
		trans-2-Pentene	c
		2-Methyl-1-butene	a,b,c
		2-Methyl-2-butene	a,b,c

Table 2-16. (Cont'd).

Carbon Number	Class	Compound	References
		3-Methyl-1-butene	c
		2-Methyl-1,3-butadiene	
	Cycloalkane	Cyclopentane	a,c
	Cycloalkene	Cyclopentene	a,c
6	Alkane	Hexane	a,c
		2-Methylpentane	a,c
		3-Methylpentane	a,c
		2,2-Dimethylbutane	a,c
		2,3-Dimethylbutane	a,c
	Alkene	1-Hexene	a
		cis-2-Hexene	a
		trans-2-Hexene	a
		cis-3-Hexene	a
		trans-3-Hexene	a
		2-Methyl-1-pentene	a
		4-Methyl-1-pentene	a
		4-Methyl-2-pentene	a
	Aromatic	Benzene	a
	Cycloalkane	Cyclohexane	a
		Methylcyclopentane	a
7	Alkane	2-Methylhexane	a
		3-Methylhexane	a
		2,3-Dimethylpentane	a
		2,4-Dimethylpentane	a
	Aromatic	Toluene	a,b

Table 2-16. (Cont'd).

Carbon Number	Class	Compound	References
8	Alkane	2,2,4-Trimethylpentane	a
	Aromatic	o-Xylene	b
		m-Xylene	b
		p-Xylene	b
9	Aromatic	m-Ethyltoluene	b
		p-Ethyltoluene	b
		1,2,4-Trimethylbenzene	b
		1,3,5-Trimethylbenzene	b
10	Aromatic	sec-butylbenzene	b

a = Neligan[34]
b = Altshuller et al.[35]
c = Stephens and Burleson[8]

All the hydrocarbons above carbon number 4 listed in Table 2-16 are found in gasoline.[34] These and the lower alkenes and acetylenes are also found in automobile exhaust gases. The lower alkanes (methane, ethane and propane) are minor constituents of auto exhaust, but constitute the major fraction of most natural gas. Stephens and Burleson have reported that the hydrocarbon composition of their samples resembled that of auto exhaust with an addition of natural gas and gasoline vapor.[8] However, samples taken in industrial areas and near the smoke plume from a brush fire have shown distinctive differences in composition which could reasonably be attributed to these particular recognized sources. Special studies such as these can be very useful in identifying the importance of various sources as contributors to air pollution by hydrocarbons.

G. REACTIVITY OF HYDROCARBONS IN THE PHOTOCHEMICAL SMOG COMPLEX

The concept that the importance of hydrocarbons and other organic substances in emissions should be related to their relative ability to cause the effects associated with photochemical air pollution has gained wide acceptance. Measurements of the manifestations of photochemical smog are of particular interest in this connection because of the relatively immediate and direct impact of these phenomena on the affected public. At the same time, chemical measurements of the accumulation of secondary pollutants, as well as their rates of accumulation and the rates of consumption of the precursors, give clues to the relative contributions of both primary and secondary contaminants in determining the course of smog development. These relationships are explored in the following paragraphs.

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Many laboratory investigations have been carried out with mixtures simulating atmospheric contaminant levels irradiated with ultraviolet light simulating the actinic fraction of sunlight. The results have indicated a need to differentiate between reactive and unreactive contaminants. For this purpose, various scales of reactivity have been devised. As a biological indicator, the potential to produce eye irritation has been a favorite subject of investigation,[36,37] while chemical scales have been based on oxidant accumulation,[38] rate of hydrocarbon consumption[39] and rate of photo-oxidation of nitric oxide.[40]

1. Biological Effects

The relation of measured eye irritation to levels of hydrocarbons and secondary contaminants is discussed elsewhere (see Chapter 1, Section B.3). In various sets of experiments it has appeared well correlated with formaldehyde concentrations, but this relation is not general. Heuss and Glasson have recently developed a reactivity scale based on eye irritation developed in a standard test, with the result shown in Figure 2-2.[37] On this scale the most reactive compounds tested were several aromatic olefins, i.e., benzene derivatives having olefinic side chains. The authors noted that eye irritation in these tests had no evident relation to various chemical measures, namely, the rate of formation of nitrogen dioxide or ozone, the maximum ozone concentration, the hydrocarbon consumed, or the formaldehyde or peroxyacetyl nitrate generated. They suggested that peroxybenzoyl nitrate might be an important contributor to eye irritation.

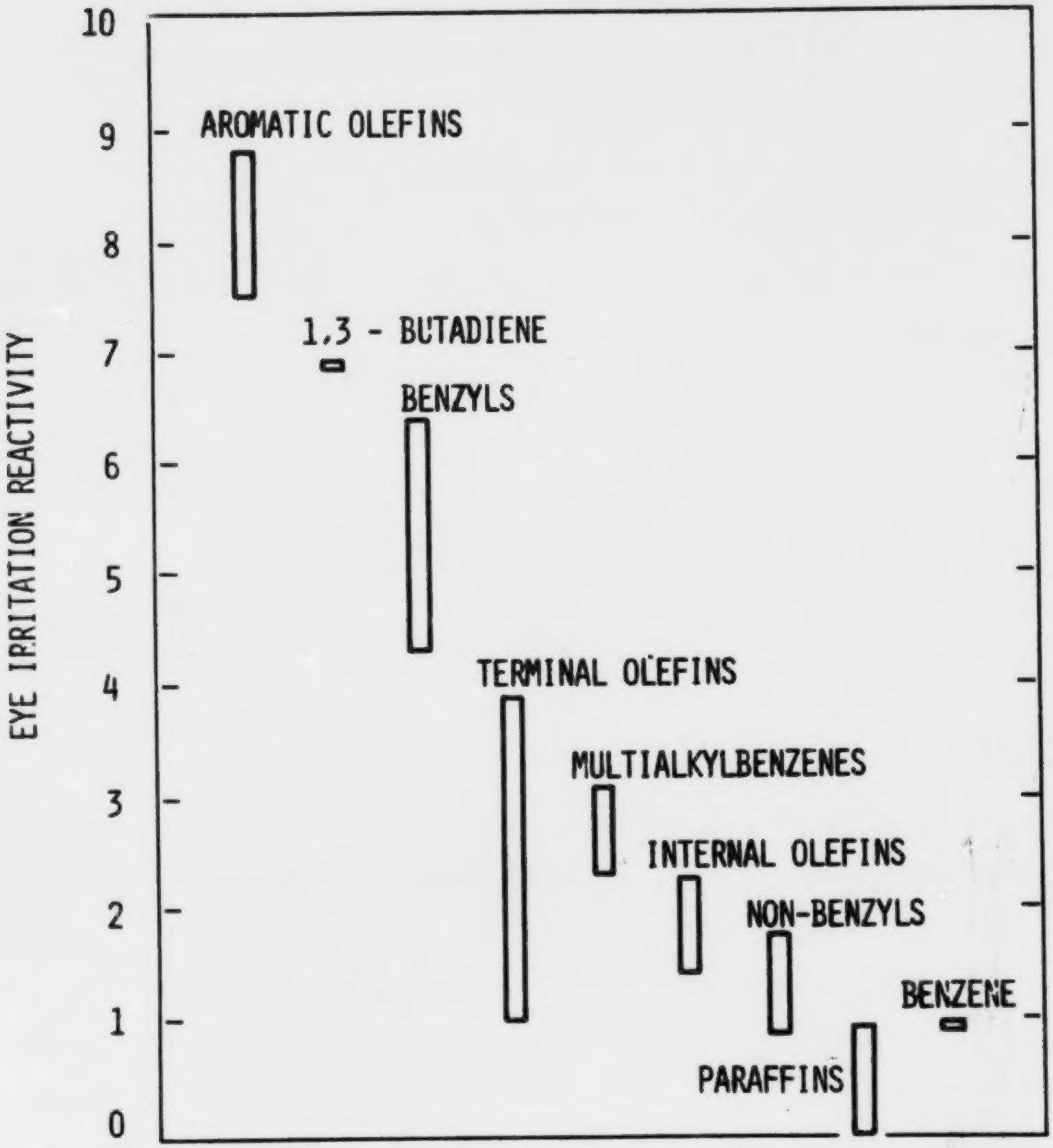

Figure 2-2. EYE IRRITATION REACTIVITY VS. HYDROCARBON STRUCTURE.[37]

Altshuller[41] concluded that olefins, alkylbenzenes and aldehydes are all responsible for biological effects, while the paraffins are considerably less reactive. Paraffins of carbon number 6 or more showed some reactivity for biological effects, but lower paraffins, together with benzene and acetylene, showed essentially none.

2. Chemical Effects

Reactivity of individual hydrocarbons in terms of chemical effects was extensively reviewed by Altshuller.[42] Measured by rate of hydrocarbon consumption, the 2-alkenes and 3-alkenes were most reactive, followed by tri- and tetra-alkylbenzenes, 1-alkenes (excluding ethylene), dialkylbenzenes, and ethylene. Considered by the same measure, aldehydes were found to be intermediate between dialkylbenzenes and ethylene. Less reactive than ethylene were toluene, then paraffins, acetylene and benzene.

A ranking based on the rate of photo-oxidation of nitric oxide to nitrogen dioxide yielded generally the same order of reactivities, but discordant results were obtained in rankings based on various measures of maximum oxidant.[42] These discrepancies probably arise from the fact that ozone has very much the character of an intermediate in the photo-oxidation system, being both generated and consumed at rates much faster than its rate of accumulation. Consequently, the ozone level is very sensitive to variations in the experimental conditions imposed in the different studies.

A specific rating scale based on rates of photo-oxidation has been set forth by Caplan,[43] with numerical estimates for various hydrocarbon classes as follows. Least reactive, Class I (specific reactivity 0), includes methane, ethane, propane, the acetylenes and benzene. Class II (specific reactivity 2) includes monoalkybenzenes, alkanes of carbon number 4 or more, ortho- and para-dialkylbenzenes, and cycloaklabes. Class III (specific reactivity 5) comprises ethylene, meta dialkylbenzenes, and aldehydes. Class IV (specific reactivity 10) includes 1-alkenes besides ethylene, alkadienes, and multialkylbenzenes. Class V (specific reactivity 30) comprises 1,2-dialkylethylenes. Class VI, most reactive (specific reactivity 100), includes tri- and tetra-alkylethylenes and cycloalkenes.

As Altshuller notes,[41] hydrocarbon consumption rates and nitrogen dioxide formation rates define reactivity scales having a much wider range than those useful for biological effects. This is probably because the biological effects depend on levels or dosages of certain contaminants rising above certain threshold values. Further, the formation of certain products can relate to details of molecular structure quite differently than do the rates of reaction.

3. Composition Indicators

To overcome the difficulties cited, Altshuller has developed a composite reactivity scale based on product yields combined with biological effects measurements.[41] Considering that precision of experimental results warranted no very broad numerical range for such a scale, he converted each type of indicator to a scale of integers from 0 to 10, thus obtaining the estimates shown in Table 2-17.

Table 2-17. INDIVIDUAL REACTIVITIES AND COMPOSITE REACTIVITY BY PRODUCT YIELDS AND BIOLOGICAL INDICATORS FOR ALIPHATIC ALDEHYDES AND HYDROCARBONS OF VARIOUS CLASSES.[41]

	Response on 0 to 10 Scale						
Substance or Subclass	Ozone or Oxidant	Peroxy-acyl Nitrate	Formal-dehyde	Aerosol	Eye Irrita-tion	Plant Damage	Averaged Response
C_1 C_5 paraffins	0	0	0	0	0	0	0
acetylene	0	0	0	0	0	0	0
benzene	0	0	0	0	0	0	0
C_6 + paraffins[a]	0-4	0[b]	0[b]	0	0[b]	0	1
toluene (and other monoalkylbenzenes)	4	ND[c]	2	2	4	0-3	3
ethylene	6	0	6	1-2	5	+[d]	4
1-alkenes[e]	6-10	4-6	7-10	4-8	4-8	6-8	7
diolefins	6-8	0-2	8-10	10	10	0	6
dialkyl and trialkyl-benzenes	6-10	5-10	2-4	+[d]	4-8	5-10	6
internally double-bonded olefins[f]	5-10	8-10	4-6	6-10	4-8	10	8
aliphatic ahlehydes	5-10	+[d]	+[d]	ND[c]	+[d]	+[d]	-

---

[a] Averaged over straight-chain and branched-chain paraffins.

[b] Very small yields or effects may occur after long irradiations.

[c] No experimental data available

[d] Effect noted experimentally, but data insufficient to quantitate.

[e] Includes measurements on propylene through 1-benzene, 2-ethyl-1-butene and 2,4,4-trimethyl-1-pentene.

[f] Includes measurements on straight-chain butenes through heptanes with double-bond in 2 and 3 position, 2-naethyl-2-butene, 2,3-dimethyl-2-butene, cyclohexene.

This sort of reactivity rating has advantages, particularly if there is to be a comparative consideration of techniques for abatement of photochemical precursor emissions involving some control of the composition of emissions. For example, on the basis of hydrocarbon consumption rates or of nitric oxide photo-oxidation rates, the control of 2-alkenes and 3-alkenes would appear to be very critical because of their high values on these scales, while the control of other alkenes and of alkylbenzenes would be expected to have a much smaller effect. Such expectations, however, are not supported by the product yields of biological indicators. Thus the Altshuller scale tends to avoid undue weighting of those compounds with high reaction rates but relatively low potential for photochemical smog manifestations.

If a reactivity scale is to have value beyond that of ranking particular compounds according to selected characteristics, one useful function would be to predict the behavior of mixtures of the rated compounds. Altshuller et al., in the course of an intensive study of the photo-oxidation of propylene, investigated the extent to which the behavior of propylene might be considered to approximate that of auto exhaust.[35] On the scale described in Table 2-17, automobile exhaust was found to have average reactivity significantly less than that of propylene--in fact, between toluene and ethylene. On the scale described by Caplan (see paragraph 2. above), the average reactivities of auto exhaust fell between ethylene and propylene. However, auto exhaust under similar experimental conditions yielded somewhat higher values of oxidant and peroxyacetyl nitrates than did propylene. The discrepancies were reduced when tests were run with less initial nitric oxide. It is evident from the comparison that pure propylene can serve as an approximate analogue for automobile exhaust in chamber irradiation studies, but only in a rather gross approximation. With a composite reactivity scale based on product yields and biological effects and having a rather limited response range, it may be possible to develop analytical procedures based on simple fractionation of the hydrocarbon contaminants for use in estimating reactivity of the atmospheric mix, or of hydrocarbons emitted from particular sources, such as auto exhaust.

H. PROPERTIES OF OXIDES OF NITROGEN

Seven oxides of nitrogen are known: N_2O (nitrous oxide), NO (nitric oxide), N_2O_3 (nitrogen sesquioxide), NO_2 (nitrogen dioxide), N_2O_4 (dinitrogen tetroxide, dimer of NO_2), N_2O_5 (nitrogen pentoxide), and NO_3 (nitrogen trioxide). Nitrous oxide is a natural constituent of the atmosphere, is not considered to be an air contaminant and is not detected by analytical methods for the other oxides. Of the remaining compounds only nitric oxide and nitrogen dioxide are directly emitted to the atmosphere.

Nitrogen trioxide and nitrogen pentoxide are thought to take part in some of the important atmospheric reactions (see Chapter 4), but equilibrium and reaction kinetics factors do not favor their accumulation to significant (or even measurable) levels. Nitrogen sesquioxide (N_2O_3) is the anhydride of nitrous acid, HNO_2, but it exists only in equilibrium with NO and NO_2, and at atmospheric concentrations of the latter [illegible] is insignificant. A summary of the physical properties of the several oxides of nitrogen is given in Table 2-18.

1. Nitric Oxide

Nitric oxide represents over 90 percent of the significant nitrogen oxides emitted to the atmosphere. It is a colorless gas, sparingly soluble in water, and boils at -151.8°C. It is formed during high temperature combustion processes according to the following endothermic reaction:

$$1/2\ N_2 + 1/2\ O_2 \rightleftarrows NO$$

The equilibrium concentration increases with rising temperature. Even though nitric oxide is unstable at ambient temperatures, the rate of decomposition is exceedingly small. Thus, as combustion gases are rapidly cooled, nitric oxide in relatively high concentration is said to exist in a state of frozen equilibrium.

2. Nitrogen Dioxide

Nitrogen dioxide exists in equilibrium with its dimer dinitrogen tetroxide (N_2O_4) according to the following equation:

$$2NO_2 \rightleftarrows N_2O_4$$

At atmospheric concentrations of nitrogen dioxide, however, the fraction present in dimer form is negligible. Nitrogen dioxide is a corrosive gas of high oxidizing power, and is important not only as the primary receptor of ultraviolet energy from the sun required in the photochemical smog reactions, but as an irritant and toxic compound. It has a characteristic pungent odor, is reddish-brown in color, and boils at 21.3°c.

Table 2-18. SOME PHYSICAL PROPERTIES OF OXIDES OF NITROGEN*

Name	Formula	Melting Point	Boiling Point	Specific Gravity
Nitrous oxide	N_2O	-102.4°C	-88.49°C	1.226
Nitric oxide	NO	-163.6	-151.8	1.269
Nitrogen sesquioxide	N_2O_3	-102	3.5	1.447
Nitrogen dioxide	NO_2	-9.3	21.3	1.491
Nitrogen tetroxide	N_2O_4			
Nitrogen pentoxide	N_2O_5	30	47	1.642
Nitrogen trioxide	NO_3	unknown	unknown	unknown

---

*From: "Handbook of Chemistry and Physics."

Only very small quantities of nitrogen dioxide are emitted directly to the atmosphere. The conditions for its formation in high-temperature combustion processes during which nitric oxide is formed are quite unfavorable, but some is emitted from chemical processes using concentrated nitric acid. Although total quantities on a nationwide basis are low, significant atmospheric concentrations are possible in highly localized cases.

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A. INTRODUCTION

The possible effects of contaminants in the atmosphere are judged against a fabric of exposure events defined by intensity (concentration), frequency, and length of exposure. Man controls these events only indirectly through activities leading to the introduction of contaminants to the atmosphere; once introduced, the fate of these contaminants is controlled by physical and chemical processes present in the environment.

The development of plans to achieve desired air quality goals requires the prediction of contaminant patterns expected as the result of possible abatement actions. This implies at least a crude understanding of the atmospheric processes acting on air contaminants. As this understanding is refined, it is expected that greater use of predictive air quality simulation models will be made. One such model and its application to photochemical air contamination is discussed in Chapter 6 of this document.

This chapter treats those atmospheric processes that are particularly important in relating the emissions of contaminants from sources to the resultant spatial and temporal distribution and concentrations of the contaminants. It is intended primarily for the nonmeteorologist who is concerned with the development of abatement strategies. As such, it deals primarily with transport and mixing processes controlled by both large-scale weather features and more localized or mesometeorological factors. The transmission of solar energy leading to the initiation of photochemical reactions is also discussed.

B. CLIMATOLOGY AND AIR MASS BEHAVIOR

The state of the atmosphere provides a primary influence on the concentration of air pollutants by prescribing the volume of air with which contaminants can mix during and after emission. When the sources of contaminants are extensive, i.e., a typical urban area, the initial dilution depends primarily on wind speed. After emission the dilution continues as the polluted volume increases in size due to mixing and stirring motions at its lateral and upper boundaries. Increase in volume depth by vertical diffusion at the upper boundary depends upon the atmospheric stability at that level. Horizontal diffusion at the lateral and upper boundaries depends upon turbulent eddy motions in the horizontal air flow, which in turn are a function of terrain, wind speed, stability, and sky cover.

Large-scale weather features, such as high and low pressure areas that influence horizontal and vertical motion of the atmosphere, can usually be recognized on conventional weather maps and charts. The pattern of occurrence of these features over a long period of time forms a record that is generally referred to as the climatology of an area. Predictions based upon these past records are valid only in a statistical or probabilistic sense. The most important of these large-scale weather features are treated in this section.

1. Atmospheric Pressure Systems

The strength of the wind depends on the horizontal gradient of atmospheric pressure. Areas with large horizontal pressure gradients are easily recognized on conventional weather maps as the place where the isobars are spaced close together. They are the site of the windy areas. The pressure gradient decreases near the centers of high- and low-pressure areas, becoming essentially zero at the centers. Here the wind is weakest, often calm. Centers of high-pressure areas (anticyclones) and low-pressure areas (cyclones) are places where dilution due to horizontal air motion is minimized. Conversely, in zones of closely packed isobars (strong horizontal pressure gradients) between the centers of cyclones and anticyclones, this type of dilution is maximized.

Most cyclones and anticyclones migrate across the United States (roughly from west to east). As a result, the strength of the wind at any one location usually varies from day to day, with consequent variation in the dilution of air contaminants. Sometimes, however, a pressure system becomes almost stationary (stagnates) for a period of some days. In this instance the area near the center is subject to very little horizontal air motion for a protracted period and pollution produced there tends to accumulate. Although this is not the case with cyclonic systems (as discussed below), it is particularly important with respect to anticyclones, which are associated with reduced vertical motion.

Korschover[1] has prepared a climatology of the occurrence of such anticyclones over the United States east of the Rockies. His results, shown in Figure 3-1, detail the sites where anticyclones tend to stall, making those sites subject to weak winds. Substantial variation is indicated, but no area can be considered truly immune from poor dispersion conditions.

2. Vertical Stability

The upper limit to the spread of pollution is determined by the vertical stability of the atmosphere. A stable layer of air is one which

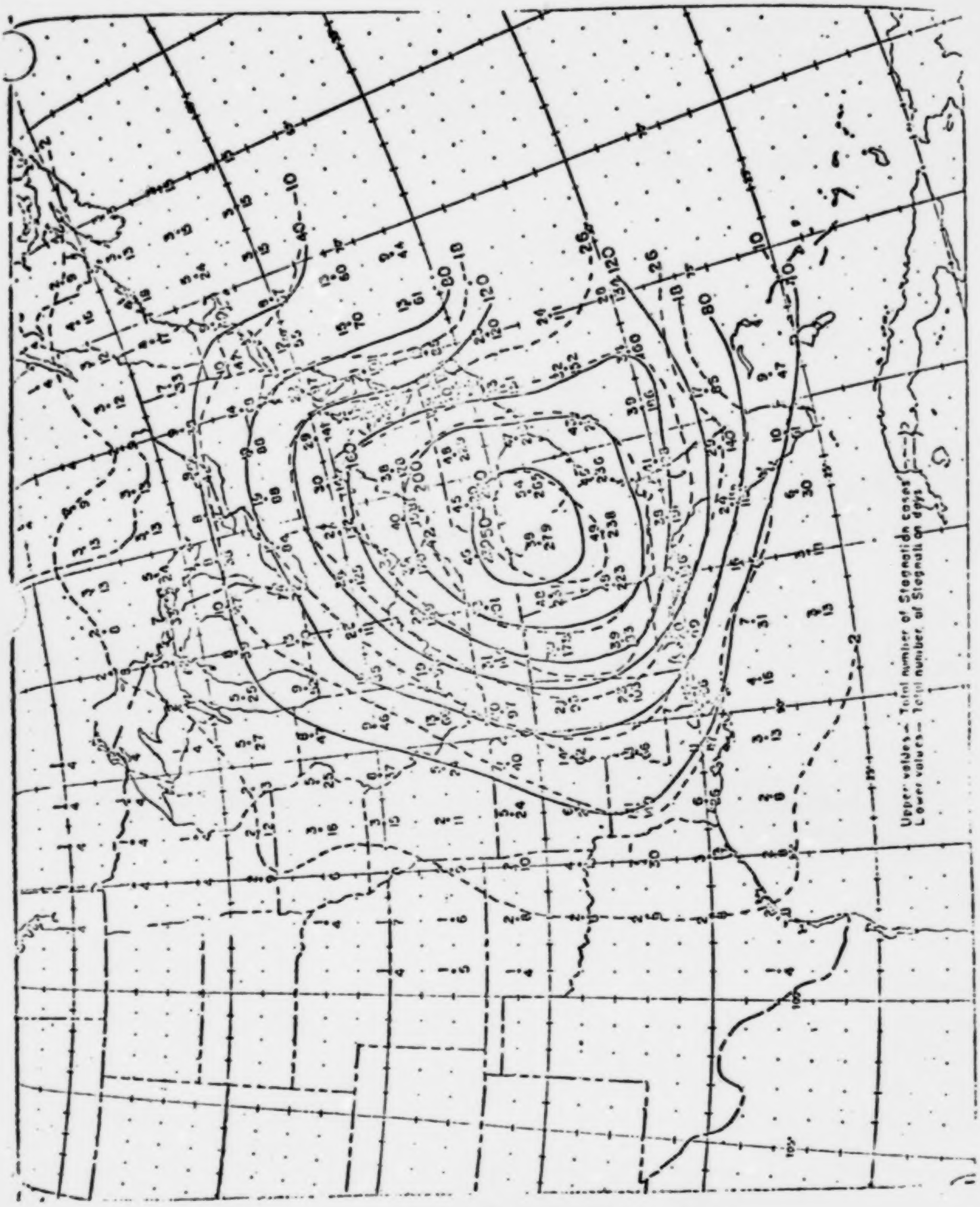
Upper values— Total number of Stagnation cases
Lower values— Total number of Stagnation days

Figure 3-1. OCCURRENCE OF ANTICYCLONES OVER THE EASTERN PORTION OF THE UNITED STATES.

resists stirring and mixing motions in vertical directions. This characteristic of the atmosphere is determined by its vertical temperature structure. When temperature increases with height through a layer of the atmosphere (temperature inversion), the layer is very stable. Typically, temperature decreases with height at a rate of about 3° F per 1000 feet. In these circumstances it is only slightly stable: the greater the decrease in temperature, the less stable the layer. Pollutants mix rapidly upward when this vertical temperature gradient exceeds 5.4° F per 1000 feet (dry adiabatic rate at cooling). Vertical diffusion, on the other hand, practically halts in the presence of a temperature inversion.

Temperature inversions are not rare and may occur almost anywhere. Nocturnal inversions form over land at ground level on clear calm nights, the air being chilled by contact with the cold ground. Provided the wind is not too strong, they also form when warm air is moved in over a colder surface (warm sea to cold land, for example). Or they can form at or above the surface when a layer of air subsides. The inversion-forming processes are discussed in detail in the following section.

Daytime heating of the ground and the layer of air next to it destroys ground inversions. For this reason the nocturnal ground inversion seldom survives the first hour or so of sunlight and normally does not possess the longevity to allow serious pollution accumulation. Advection (horizontal transport) of a low inversion layer from a cold surface to a warm surface also can eliminate an inversion. This happens (but usually too late to prevent build up of contaminants) when air moves from the Pacific across the Los Angeles coastal plain to the interior deserts. One further mechanism that can destroy an inversion in an atmospheric layer is the vertical stretching (deepening by being squeezed horizontally) of the layer. This type of motion is typical in the lowest layers of a cyclone and explains why air pollution episodes are rare at the center of cyclones despite relatively sluggish air motion.

Daytime heating by increasing the temperature of the layer of air next to the ground erodes inversion layers from below, sometimes completely destroying them. During this process the lowest layer of the atmosphere, through which ground-produced air pollution is allowed to mix, becomes deeper and deeper. This depth, called the mixing depth (frequently referred to as mixing height), reaches a maximum about the time maximum air temperature is reached at ground level (usually sometime in the afternoon). Since this depth is a measure of the maximum vertical pollution mix during the entire day, it is a variable directly related to maximum dilution. Holzworth[2,3] has developed statisticl for maximum mixing depth over most of the United States. Figure 3-2 shows the mean mixing depths over the Western United States for four different months using a contour interval map. Month by mean morning and afternoon mixing heights for four widely separated cities are shown in Figure 3-3[4]. The wide seasonal, geographical, and daily variations in this parameter are evident from these figures.

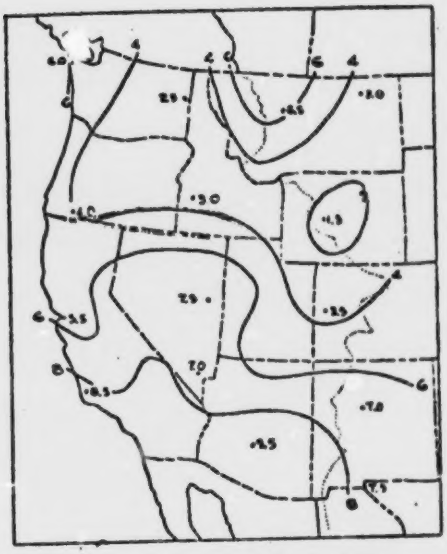

Figure 3-2a. January mean maximum mixing depths in hundreds of meters above the surface, computed from mean radiosonde observations (1946-1955) and mean maximum surface temperatures (1921-1950). Contour interval 200m.

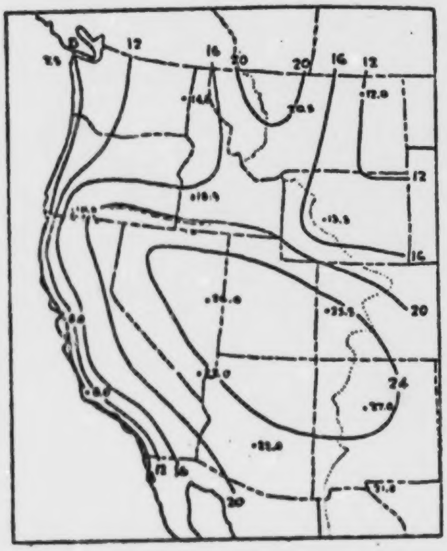

Figure 3-2b. Same as Figure 3-2a, but for April. Contour interval 400m.

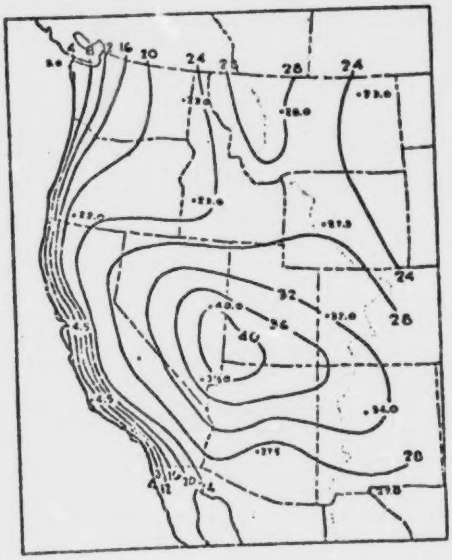

Figure 3-2a. Same as Figure 3-2a, but for July. Contour interval 400m.

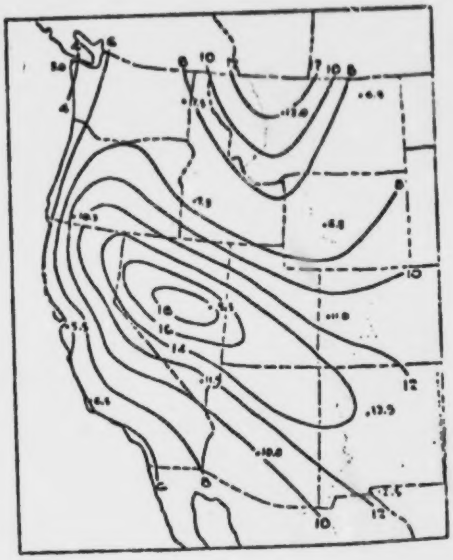

Figure 3-2d. Same as Figure 3-2a, but for October. Contour interval 200m.

Figure 3-2. **MEAN MIXING DEPTHS FOR THE WESTERN UNITED STATES.**

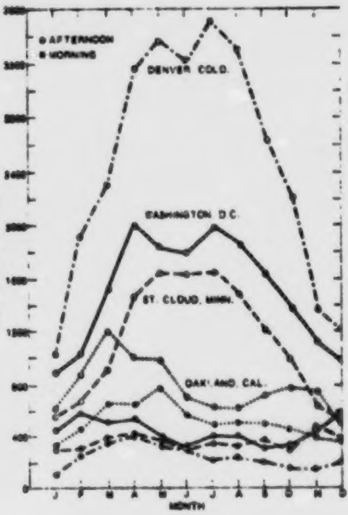

Figure 3-3. MONTHLY MEAN AFTERNOON (OPEN CIRCLES) AND URBAN MORNING (SOLID CIRCLES) MIXING HEIGHTS. ALL DATA FOR 1960-1964, EXCEPT WASHINGTON FOR 1961-1964.

C. TRANSPORT AND DISPERSION

Within the limits imposed by the large-scale features of the atmosphere, the transport and dispersion of air contaminants depends greatly upon the more localized and detailed structure and motion of the layer of air involved. As a cloud of pollution moves it mixes with its atmospheric environment. Two types of mixing or diffusion take place simultaneously: molecular diffusion and eddy diffusion. However, the rate of transfer of material across the cloud boundary by individual molecular motions is negligible compared with that generated by eddy motions.

The eddying motion of the atmosphere encompasses a wide range of eddy sizes, from the small wisp traced by the smoke from a cigarette to the considerably larger whirls, cyclones and anticyclones that may be a thousand miles in diameter. The diffusion rates stemming from these widely disparate scales are themselves grossly different, with values that range over more than ten orders of magnitude when computed for the whole spectrum of motions in the atmosphere. As a consequence, clouds of pollutants that are injected into the atmosphere are observed to disperse and diffuse at rates that increase markedly as the clouds themselves increase in size. This is because the scale of mixing motions that can exist completely interior to clouds naturally increases as the clouds become larger.

Thus, atmospheric motions on a scale that is small compared to the cloud actively mix the cloud with its environment (diffusion). Motions on a scale large compared to the cloud bodily move the entire cloud (transport), and motions on a scale comparable to the cloud merely change its shape (deformation). A cloud may thus pass through a long history from small, simple, concentrated volume to very large, complicated and dilute volume. These transformations are accompanied by a continuing enhancement of the dilution mechanism as each larger and more effective scale of eddy leaves the ranks of the transporting motions and joins those actively diffusing--and therefore expanding--the cloud.

In the case of a continuous source of contamination, this process produces an ever-widening plume of pollution moving off downwind in ever-larger meanders. The plume becomes too dilute to detect visually long before eddying motions large enough to be represented on current weather maps become active diffusers of the plume.

On the usual weather map, data points are separated by 50 to 100 miles. A very dense mesometeorological network of wind-reporting stations is required to represent just the initial transporting and deforming flow patterns of the polluted air mass from a large city. Streamline analyses of such data sometimes delineate eddies and whirls 10 or 15 miles in diameter, such as the one in Los Angeles illustrated in Figure 3-4. Most of the eddies responsible for dilution are smaller than this, affect only one station at a time, and so go completely undescribed even on the mesometeorological streamline map. They are detectable, however, in another type of wind record: the continuous wind speed and direction traces of the individual anemometer and wind vane. These traces show the apparently random fluctuations of the wind at a

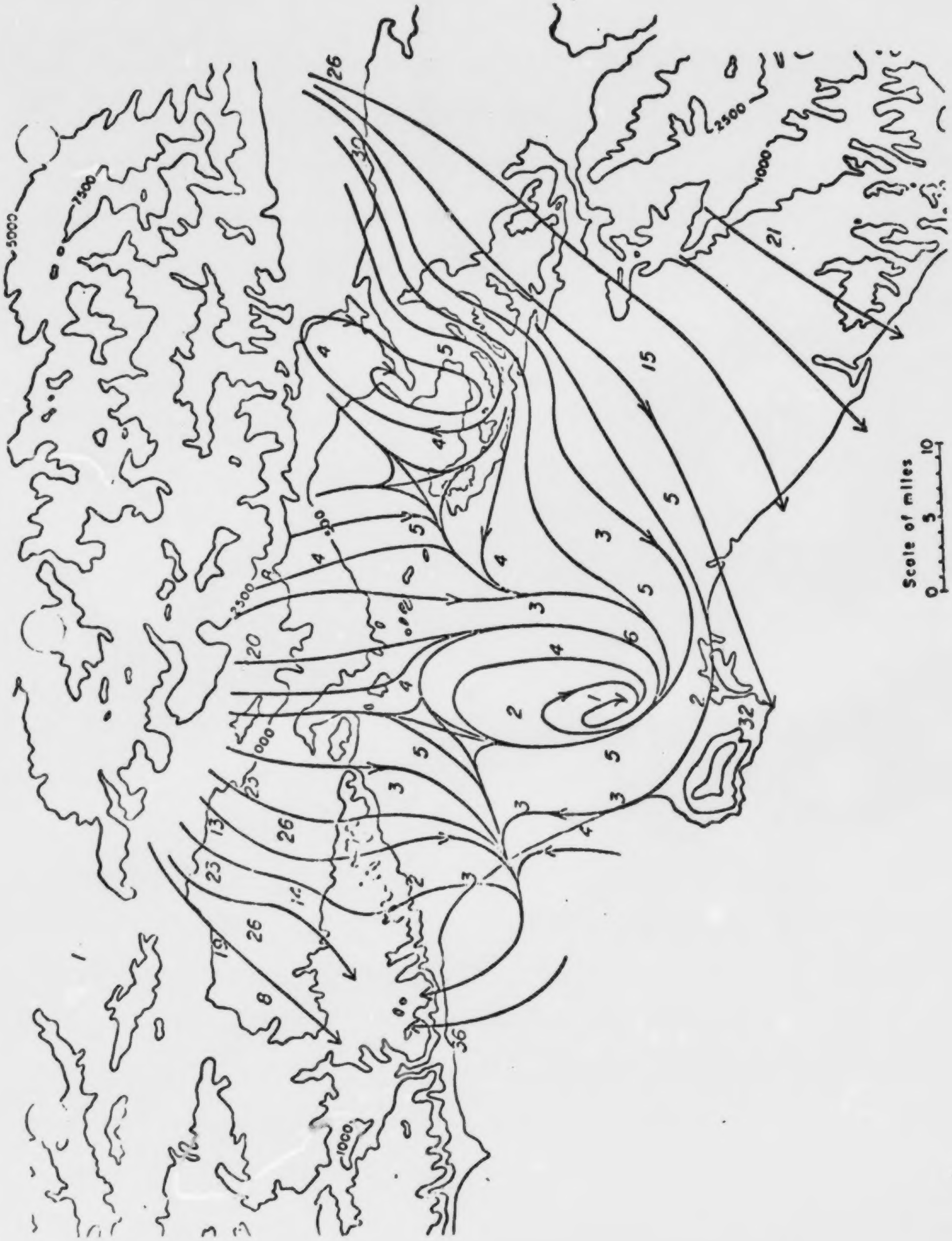

Figure 3-4. EXAMPLE OF STREAMLINE ANALYSIS FOR LOS ANGELES SHOWING MESOMETEOROLOGICAL SCALE EDDY.

single station as the atmosphere's wide spectrum of eddies drift by. Statistical descriptions of this turbulent flow (e.g., standard deviation of wind direction fluctuations) are used by the practitioner in estimating diffusion rates.

1. Diffusion and Diffusion Models

Substantial efforts are under way to produce useful atmospheric simulation models for predicting effects of various abatement strategies on air quality. The more advanced models take into account both point and area sources, variations in source strength, turbulent diffusion, transport, and atmospheric reactions.

The fundamental background of these models lies in diffusion submodels, essentially all of which are based upon the statistical theory of turbulent diffusion where a Gaussian distribution of plume spread is assumed. Turner[5] summarizes a great deal of the early work in this field and provides a useful working manual as well. The equations used for illustration here are taken from his work.

The concentration, x, of a gas or suspended aerosol at a point represented by the coordinates x, y, z downwind of a continuous point source of effective elevation, H, is given by the following equation when $z = 0$ (i.e., ground level concentration):

$$x\ (x,y,o,H) = \frac{Q}{\pi\sigma_y,\sigma_z} \exp\left[-1/2 \left(\frac{y}{\sigma_y}\right)^2\right] \exp\left[-1/2 \left(\frac{H}{\sigma_z}\right)^2\right]$$

where Q = mass emission rate

σ_y = plume standard deviation in horizontal plane

σ_z = plume standard deviation in vertical plane

μ = mean wind speed

A number of assumptions are made in this expression: (1) there is continuous emission from the source, so that diffusion in direction of the source can be neglected; (2) the material is a nonreactive gas or aerosol with negligible settling rate; (3) the plume content is conserved, i.e., there is total reflection from the ground.

Modifications of the general form of this equation have been derived for estimating seasonal or annual concentrations, area and multiple source concentrations, maximum downwind concentrations and a variety of other special applications.

It is evident from the foregoing that the utility of the diffusion equation is limited by the ability to obtain accurate estimates of the plume standard deviations, σ_y and σ_z. Some problems may be encountered in obtaining H, the effective release height, when plume rise must be considered, but the other parameters are fairly straightforward. Values of σ_y and σ_z vary in a complex way with the vertical temperature structure of the atmosphere, wind speed, roughness of the earth's surface and distance from the source. Simplified methods have been developed to estimate these parameters from normally available mesometeorological data such as wind speed and vertical stability[4].

2. Vertical Temperature Structure

Whether the prediction of air quality in a given area from defined sources is accomplished through the use of simulation modeling or by purely statistical methods such as multivariate analysis, the buoyancy-induced turbulence related to vertical temperature structure is worthy of additional discussion.

If a parcel of air is rising relative to the air around it, one of two events may be responsible: The parcel may have encountered an obstacle and been deflected upward, or it may have become buoyant. The mixing motions that result when air moves over uneven terrain are mainly confined to the layer next to the ground. Buoyancy effects, on the other hand, are not confined to the lowest boundary of the atmosphere and are the basic cause of most vertical mixing throughout the depth of the lower atmosphere.

A hypothetical layer of air which is isothermal, i.e., has the same temperature at all heights, can be considered as an example. A small parcel of air interior to the layer, lifted 1000 feet through the layer, would be surrounded by air at the same temperature as its original environment. However, the temperature of the parcel would have decreased by adiabatic expansion while moving upward to a position of lower pressure. If no heat were gained (or lost) by the parcel in the process, it would have cooled at the dry adiabatic rate, 5.4° F per 1000 feet (1° C per 1000 meters) by virtue of expanding against its environment. Being 5.4° F cooler than its new environment, it would be negatively buoyant at this position and, if released, would fall back to its original level. On the other hand, the parcel, through compressional heating, would become positively buoyant by displacement downward; released it would rise again, seeking its original level. We must therefore conclude that an isothermal layer is stable to the vertical displacements of all parcels within it. Vertical mixing motions are opposed by restoring buoyancy forces, and resulting diffusion rates are small.

Usually the lowest layer of the atmosphere is not isothermal. Typically it is stratified so that the temperature at one level is about 3° F cooler than it is 1000 feet lower, i.e., it has a "lapse" in temperature of 3° F per 1000 feet. Above its original level a displaced parcel again is cooler than its new environment, but this time only by 2.4° F. Again there is a restoring force, but it is much smaller; therefore, this layer is neither as stable nor as resistant to vertical mixing motions as an isothermal layer.

In an atmospheric layer whose lapse rate numerically equals the dry adiabatic rate of cooling, vertical displacements develop no buoyancy forces at all. Such an atmospheric layer has neutral stability. Since the vertical motions are unopposed by buoyancy forces, diffusion rates are high.

In a layer whose lapse rate exceeds the dry adiabatic rate of cooling (for example, 7° F per 1000 feet), an upward displacement of 1000 feet results in a parcel 1.6° F warmer than its environment. In this case there is no restoring force. Instead there is a force in the direction of the displacement, and the further the air parcel moves from its initial position the greater the buoyancy force in that direction. This layer is unstable to vertical displacements. Unstable layers have high diffusion rates, and the greater the lapse rate the greater the diffusion.

To summarize, one property of the atmospheric layer that determines the rate of atmospheric diffusion within the layer is the vertical termperature gradient. This is classified as stable, neutral, or unstable in order of increasing potential for diffusing pollutants (see Figure 3-5).

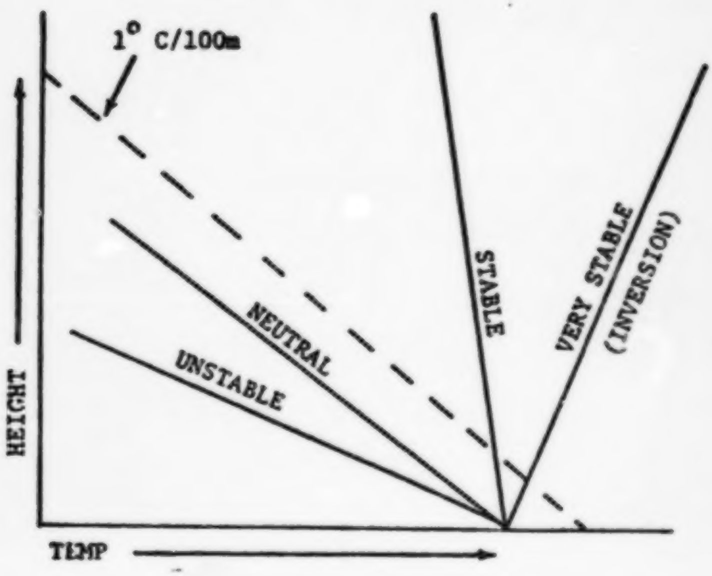

Figure 3-5. RELATION OF TEMPERATURE AND HEIGHT TO ATMOSPHERIC STABILITY.

Of interest is the most stable configuration, the inversion, in which temperature actually increases with height. Inversion layers are so successful at suppressing vertical mixing (have such small diffusion coefficients) that in most cases they effectively halt the vertical transfer of pollution. A combination of large-scale and local weather conditions determines when and where inversions are formed. When these conditions either cool a layer of air from below, heat it from above, or both, they produce an inversion in the layer.

For the lowest layer of the atmosphere, cooling from below is usually caused by nighttime radiation losses at or near the ground. These are most pronounced when the sky is clear (no radiation back to the ground from the clouds) and when the wind is light (a minimum of mechanical mixing transferring heat from warm air above to cold air below). Under such conditions very marked inversion layers, usually a few hundred feet in depth, develop at the surface. Inversions that form in this way are called radiation inversions.

Another way in which air can be cooled from the bottom is by moving horizontally from a warm lower boundary to a cool one, coastline to a cool ocean. Eddy diffusion transports heat from the air to the ocean, cooling the lowest part of the atmosphere.

Heating a layer from above invokes less obvious processes. Only one, adiabatic compression, is of importance. It occurs when a layer of the atmosphere becomes shallower. For example, if a volume of air next to the ground spreads out horizontally, it must at the same time get shallower. The air at the top is heated by compression as it descends, but the air at the surface remains at the same elevation and is unheated. This sort of deformation of air volumes is called subsidence and tends to stabilize the layer; if carried far enough, it will produce a temperature inversion in the layer. As mentioned earlier, subsidence is associated with anticyclones: Air tends to spiral out away from the centers of these high pressure areas, producing a divergence of the air flow which is automatically accompanied by sinking of the air over the anticyclone. The presence of an anticyclone over the eastern United States for a protracted period set the stage for the well-known air pollution disaster at Donora, Pennsylvania in 1948, and the large semipermanent anticyclone off the coast of California provides Los Angeles with its persistent summer inversion.

When the weather situation provides the opposite of the inversion-producing processes (cooling from above and heating from below), an inversion, if present, is destroyed. Cooling aloft occurs when the atmosphere is stretched in the vertical (the opposite of subsidence). This is generally the case in the vicinity of cyclonic storms and accounts, in large part, for the accompanying comparative lack of low inversions. Heating from below as the hot ground passes heat to the air is a regular daytime occurrence over land in the absence of clouds, and accounts for the rapid weakening--if not complete destruction--of low inversions during the day.

3. Transport

Horizontal air motions also play an important role in the dilution and transport of atmospheric contaminants. For example, in a large metropolitan area on a day when a low, strong inversion exists, the inversion may be so stable that it effectively damps out all vertical mixing motion at its level. Although vigorous mixing motions may exist in the less stable--perhaps even unstable--layer between it and the ground, the inversion imposes an upper limit on this eddy diffusion. Pollution introduced at the ground becomes diluted with the subinversion air, but the absence of vertical mixing motions in the inversion layer itself prevents any further penetration of the contaminants in the vertical.

In the absence of any horizontal motion, the urban environment would constitute a large area source continually pouring pollution into a fixed volume delineated by the periphery of the source area and the depth of the subinversion layer. As long as conditions remained unchanged, pollutant concentrations would continue to mount in this fixed volume of air. The obvious and most important effect of horizontal air movement is to bring new, unpolluted air over the source area and at the same time remove an equal volume of polluted air on the downwind side. Any such net transport of air across the source area puts an end to the unlimited increase in pollutant concentration in the cloud. For any given wind speed and time interval there is a prescribed volume of air into which the area source can inject contaminants; an increase in wind speed increases that volume and reduces the pollutant concentration.

For a large city these considerations yield a rather simple picture for the most important pollution situation for photochemical smog: the day with the low, strong temperature inversion. The cloud of pollution produced by the multitude of individual sources--some fixed, some moving, some continuous, others intermittent--is one fairly continuous pall over the city, stretching out downwind of it with a sharply defined upper boundary. A knowledge of the mean wind speed, the height of the base of the inversion layer, the diameter of the source area and the pollutant emission rate would permit a first approximation of the mean concentration of contaminants in the cloud, providing that chemical or mechanical removal of the contaminants remained negligible and the terrain was suitably flat. The local terrain, however, typically impresses important diurnal fluctuations on air motions and a variety of other constratints that complicate the horizontal and vertical flow field. These can lead to important distortions of the simple picture above.

4. Terrain Effects

The most obvious effect of terrain on horizontal air motions is to direct and channel the air flow, much as mountain ranges prescribe the course of rivers. Although this analogy is far from perfect, its applicability depends on the stability or instability of the atmospheric layer in question. If the layer of air covering the terrain has an unstable lapse rate, air encountering a mountain will more readily move up and over the obstacle than deviate from its course horizontally, since vertical displacements aid positive buoyancy forces. On the other hand, air within a stable layer develops opposing buoyancy forces when displaced vertically, and does behave very much like a river in mountainous terrain.

It is popular to ascribe the accumulation of smog in the Los Angeles Basin to this effect: "the damming or trapping of the smog by the encircling mountain ranges." But this cliché resembles reality only part of the time: during the hours of darkness, cooling takes place from below, creating stability and thus enhancing the channeling effects of major terrain features.

In the daytime, however, the layer of air next to the mountain is heated from below, becomes unstable, and moves upslope along with any entrained air contaminants. Far from being a dam, the slopes become a vent for the polluted lower layer during the day.

Terrain also plays a part in determining the rate at which fresh air is brought in over the source. Winds typically are not constant but have a diurnal fluctuation--a cyclic variation geared to the coming and going of the sun and instigated by differences in heating and cooling of various terrain surfaces. Undoubtedly the largest disparity in terrain as regards temperature variations is a coastline. Temperature contrasts across a coastline during a clear day set in motion a large convection regime that at ground level produces a sea-breeze (wind directed from sea toward land); at night the temperature gradient is reversed, resulting in a land-breeze in the opposite direction.

Normally this fluctuating wind is superimposed on the large-scale flow provided by pressure patterns seen on conventional weather maps. The result is an oscillatory perturbation of this general flow. In Los Angeles in summer, for instance, the general flow is from sea toward land. During the day the sea-breeze enhances this flow and at night the land-breeze opposes it. The result is on-shore movement of around 10 mph during the warm parts of the day and very nearly calm or very weak land-breeze at night. Figure 3-6 shows the halting paths taken by two arbitrarily chosen parcels of air as they moved across the Los Angeles Basin, illustrating that the afternoon provides hours of good ventilation but the early morning is a period of near stagnation. Under such conditions the source area should produce a more dilute polluted wake in the afternoon under the benevolent influence of the sea-breeze than it does in the early morning hours, when virtually no new air is brought in over the source area. This should cause an accumulation of contaminants that stops only with the midmorning onset of the sea-breeze.

Diurnal variation in ventilation can also occur in the absence of coastlines as, for example, in valley-mountain regimes. The thermal contrast producing these winds is that between the alternately heated and cooled slopes of mountains and the air at the same level out over (and well above) the valley floor--air, out of contact with the ground, that is scarcely heated or cooled at all. Figure 3-7 illustrates these daytime up-valley and up-slope flows and nighttime down-valley and down-slope winds for a valley in western Argentina. In those important instances where the large-scale pressure patterns prescribe weak flow, these diurnal wind fluctuations provide whatever horizontal ventilation an area receives.

D. TRAJECTORY ANALYSIS

The horizontal movement of air provides more than a dilution volume for air contaminants: it defines the path, or trajectory, of a diffusing air parcel according to the large-scale mean wind field. In the dynamic sense the continuing summation, over all sources, of the contaminant loadings

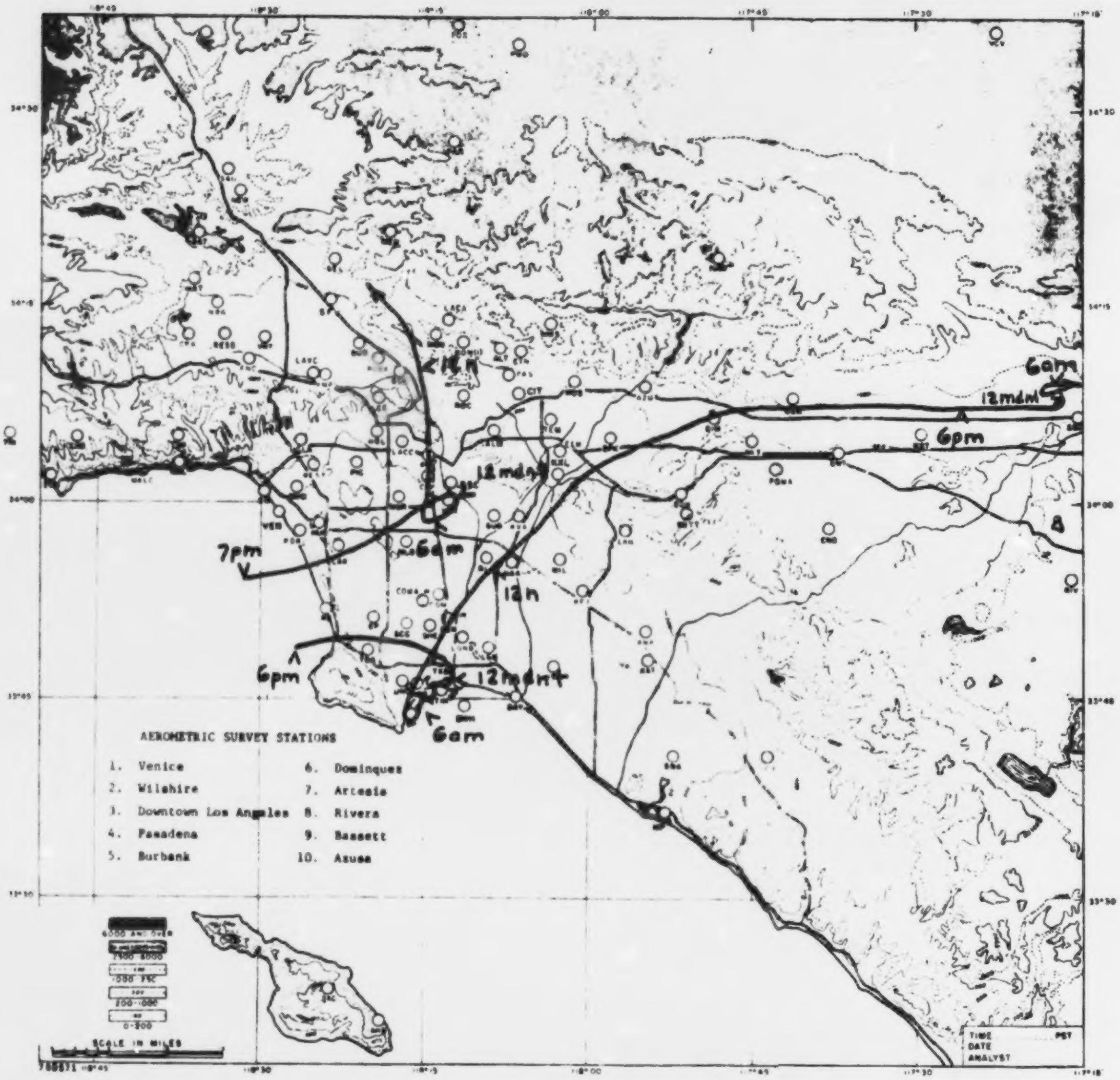

Figure 3-6. TYPICAL SUMMER TRAJECTORIES ACROSS THE LOS ANGELES BASIN.

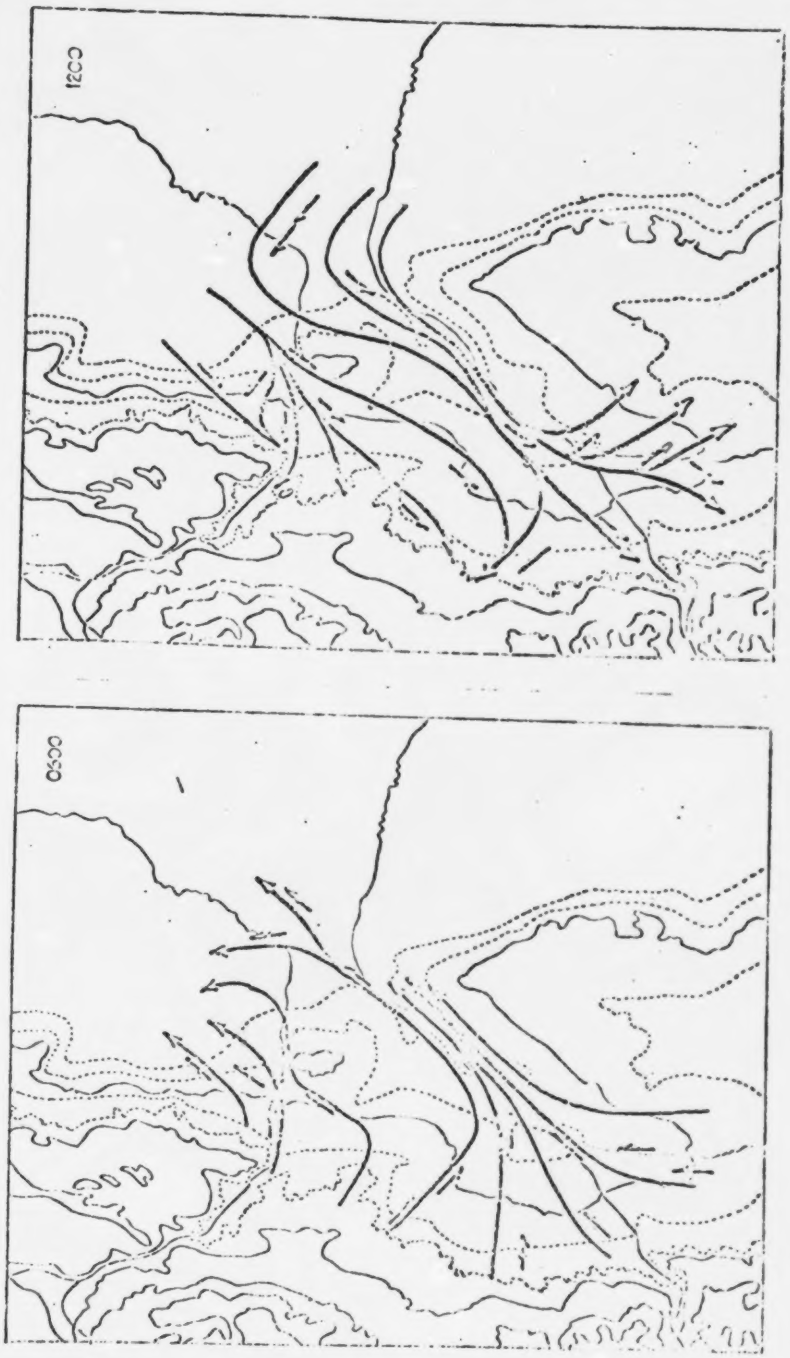

Figure 3-7. PREVAILING SURFACE WIND PATTERNS FOR 6 AM AND 12 NOON IN THE TUNUYAN VALLEY, ARGENTINA.

resulting from diffusion and large-scale transport of emissions sets the air quality for a region having well-defined boundaries. Even here we neglect losses due to reaction or escape from the system.

To account for the large-scale movement of air parcels some effort has been devoted to methods of trajectory construction from readily available wind speed and direction data. Both manual and computer-based techniques have been used. In practice, manual trajectory construction involves the analysis of air flow over the area of interest by means of a series of maps, each one representing the wind pattern at a specific time. Streamlines of wind flow (lines everywhere parallel to the wind direction) are developed on the basis of the wind direction plotted at each observational station location[6]. Wind speeds are also plotted. In most cases, hourly maps are constructed. The trajectory is developed by moving the point representing a simulated air parcel in the direction of the wind at the speed indicated by the streamline map[7]. This process is carried on over a series of maps, so that each hourly wind pattern makes its contribution to the path of the parcel, as would be the case if the parcel were actually a part of the air mass under study. Figure 3-8 shows how this method is performed.

The process of trajectory construction can be carried on both forward and backward in time. That is, air leaving a specific point is tracked forward in time as it moves from source to receptor, or, starting at a point of reception, the prior history of a parcel of air is determined by going backward in time via the appropriate series of wind streamline maps. The example in Figure 3-8 demonstrates the first case, where air leaving a specific point is tracked as it moves with the wind, until it is carried out of the area under study.

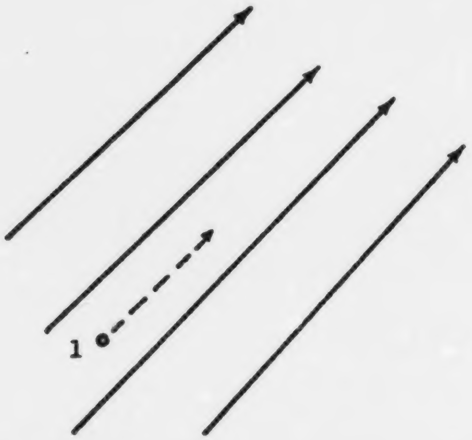

Figure 3-8a. T + 1
Path of air parcel due to air movement at time T + 1.

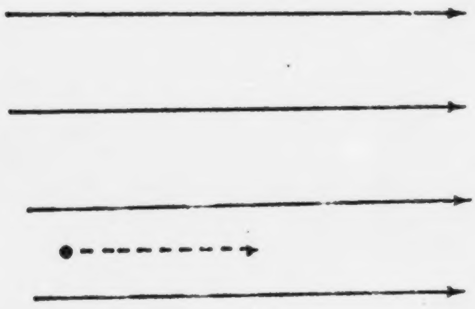

Figure 3-8b. T + 2
Path of air parcel due to movement at time T + 2.

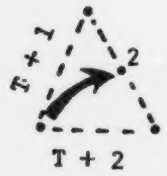

Figure 3-8c. Trajectory movement, average conditions, T + 1 and T + 2. Location of parcel at point 2 is due to graphical averaging of movement due to wind-flow maps covering time period T + 1 to T + 2.

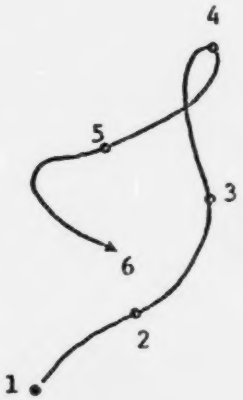

Figure 3-8d. Resulting trajectory, carried over a series of time steps.

Figure 3-8. METHOD OF CONSTRUCTING TRAJECTORIES USING STREAMLINE MAPS.

A reasonably dense wind station network is required for construction of air parcel trajectories using the analysis techniques described. Approximately seventy stations are shown in the 60- x 60-mile grid system used by Davidson, et al.[8] in the New York City area, while about fifty stations are used by the Los Angeles Network[9] in an area of about 1500 square miles.

Questions regarding the accuracy of trajectories obtained through streamline map techniques have been raised from time to time. For example, how representative of the movement of air parcels is the surface wind? Inasmuch as parcels are also being moved in the vertical, the net movement may well be the result of winds aloft rather than just those at the surface.

Studies to verify trajectories have generally taken two forms. The first measures the wind variation with height, to determine how much difference exists in wind flows within the lower atmosphere's mixed layer. If such winds do not vary greatly, the use of surface winds can be justified. Such was the conclusion of a vertical wind study[10] in the Los Angeles Basin. Tail-method pilot-balloon observations were used to determine the winds aloft in these studies.

The second method involves inserting tracer material into the air and, through a network of sampling stations, determining its location at a future time. This technique, widely employed to analyze the diffusive character of an air mass, obviously also provides information about the actual trajectory of the tagged air parcels[11].

Currently, fluorescent dusts are most often used for relatively short-distance tracing. A mineral powder, usually a zinc-cadmium sulfide, is dispersed so as to produce an aerosol cloud. The finely divided material is carried with the wind, and thus fulfills the requirement of an air tracer. Detection is accomplished by use of an ultraviolet light source shining on the sampling surface. The tracer material, of known fluorescent properties, can be identified even in the presence of other dusts[12]. Another tracer system using sulfur hexafluoride has been developed by the National Center for Air Pollution Control[13]. This method shows favorable results as compared with the fluorescent particle technique. It is especially recommended for tracing air movement over longer distances, since good results have been achieved in the range of 100 miles or more from the release point.

Another form of an air tracer is the airborne balloon. So-called "no lift" balloons may be released and their positions tracked visually or by radar through use of reflecting surfaces attached to the balloons. An assumption is made that these balloons have no excess buoyancy, and therefore respond only to the motions imparted by the air mass in which they are released[14].

A variation of the balloon trajectory technique involves the use of nonexpandable balloons, inflated with helium so that they will float at a preselected density level. Because of their characteristic tetrahedronal shape these balloons are known as "tetroons," and have been used to determine trajectories at various locations[15,16,17].

No matter how obtained, any trajectory represents only the path taken by one parcel initially positioned at a specific time and place. There is no assurance that another trajectory starting at the same place but at another time would be similar. Therefore, to make any judgment as to the frequency of occurrence of air parcel movement of a particular nature, it is necessary to replicate the trajectory-determining process many times.

The product of this process is a climatology of air parcel movements. The most frequent path may be thought of as the most frequent or "prevailing" trajectory, analogous to the concept of "prevailing" wind. To predict the most probable path air pollution will take in going from source to receptor, it is necessary to have sufficient trajectory determinations on which to base a statistical judgment. Computer-derived trajectories make it convenient to obtain such information in volume, as has been done in Los Angeles[9]. The single air pollution episode, however, requires only information related to the actual time of occurrence; in this situation, the single trajectory is sufficient to relate source to receptor.

E. SOLAR RADIATION

A major element in the study of photochemical air pollution is the effect of solar radiation on the initiation of photochemical reactions. These reactions are discussed in Chapter 4 of this document.

That region of the solar spectrum important in the primary energy-absorbing processes (i.e., 3000 to 4000A) varies regularly in intensity at the earth's surface according to season and time of day. It also varies with latitude and presence of attenuating species in the atmosphere. Information on this atmospheric factor is needed for any complete ambient photochemical air pollution study.

1. Actinic Irradiance

The light available in urban atmospheres for the promotion of photochemical reactions includes, but is not limited to, the light transmitted directly from the sun. An appreciable proportion of the light scattered out of the direct beam of sunlight still reaches the surface of the earth, and this accounts for the brightness of the sky. Under some conditions, such light from the sky may exceed that direct from the sun. Since scattering is quantitatively more important for the shorter wavelengths, its effects on the photochemical smog reaction system cannot be neglected.

Actinic irradiance can be defined as the photon flux through a horizontal unit surface. In a weakly absorbing medium (such as a polluted urban atmosphere), the rate of absorption for light of any wavelength is proportional to the concentration of the absorbing material and to the actinic irradiance for that wavelength. A useful estimate of actinic irradiance in terms of the factors discussed above is given by Leighton[18].

$$J_\lambda = I_{o\lambda} T_{a\lambda} [T_{s\lambda} + gi(1-T_{s\lambda}) \cos z],$$

where

$I_{o\lambda}$ = incident radiation intensity at the top of the atmosphere

$T_{a\lambda}$ = transmissivity (fraction transmitted) directly through absorbing layer

$T_{s\lambda}$ = transmissivity due to combined scattering and diffusion

g,i = semiempirical parameters representing particular aspects of the geometry of the scattered light

z = solar zenith angle

Table 3-1 shows values of J, calculated by this equation, for 100A (10 nm) wavelength bands through the ultraviolet and visible regions of sunlight, for a series of values of z. Figure 3-9 displays values of J for several wavelengths as a function of solar altitude, while Figure 3-10 shows the diurnal variation of J_{3700} as estimated for various latitudes at the summer and winter solstices. Within the latitudes of the contiguous forty-eight states, as Figure 3-10 shows, there is little variation with respect to either the maximum actinic irradiance (at 3700A) or the integrated 24-hour value at the summer solstice. However, at the winter solstice, the effect of latitude on these parameters is quite great. At other times of the year, of course, the latitude effect is intermediate, with the greatest variation between summer and winter at the higher latitudes. For reference purposes, the three latitudes shown are approximately those of London, Los Angeles, and Mexico City.

2. Effect of Smog on Atmospheric Transmission

Measurements by Stair[21], taken during a severe episode of smog in Pasadena, California, showed clearly that transmission of the direct solar beam was sharply reduced at wavelengths approaching 3000A. This effect is illustrated by Figures 3-11 and 3-12, both from Leighton[18]. The effect at wavelengths between 3200 and 5000A was well represented by the empirical equation

$$S_{P\lambda} = 0.133\lambda^{-1.5}$$

where

$S_{P\lambda}$ = attenuation coefficient of the polluted layer

Table 3-1. ESTIMATED ACTINIC IRRADIANCE IN THE LOWER ATMOSPHERE.

λ (A)	$J_\lambda \times 10^{-14}$, photons (cm^{-2} sec^{-1} 100 A^{-1}) at z =				
	0°	20°	40°	60°	80°
2900	0.0014	0.0009	0.0002	—	—
3000	0.12	0.10	0.05	0.01	—
3100	0.65	0.60	0.43	0.13	0.01
3200	1.17	1.10	0.91	0.53	0.10
3300	1.83	1.75	1.48	0.96	0.26
3400	1.88	1.82	1.55	1.05	0.32
3500	2.06	1.98	1.72	1.18	0.36
3600	2.10	2.02	1.77	1.24	0.38
3700	2.48	2.40	2.11	1.50	0.46
3800	2.36	2.28	2.02	1.45	0.44
3900	2.20	2.13	1.90	1.38	0.42
4000	3.10	3.01	2.70	2.00	0.62
4100	4.01	3.90	3.51	2.63	0.82
4200	4.06	3.95	3.57	2.71	0.86
4300	3.86	3.76	3.42	2.62	0.85
4400	4.50	4.39	4.02	3.11	1.03
4500	5.00	4.88	4.48	3.51	1.19
4600	5.00	4.89	4.50	3.56	1.22
4700	5.13	5.02	4.64	3.68	1.30
4800	5.20	5.11	4.72	3.79	1.38
4900	4.88	4.78	4.44	3.59	1.33
5000	4.95	4.85	4.51	3.68	1.40
5250	5.14	5.05	4.73	3.91	1.56
5500	5.30	5.21	4.90	4.09	1.69
5750	5.32	5.23	4.92	4.14	1.78
6000	5.32	5.24	4.95	4.21	1.86
6250	5.27	5.19	4.94	4.25	2.01
6500	5.22	5.16	4.92	4.30	2.16
6750	5.16	5.10	4.89	4.32	2.29
7000	5.05	5.00	4.82	4.29	2.38
7500	4.80	4.75	4.59	4.10	2.47
8000	4.55	4.51	4.37	3.98	2.47

* Values given are from equation (II-37), with $I_{0\lambda}$ from Table 1, T_a from Table 4, and T_{sa} from equation (II-13). Parameters employed are $P = 1000$ mb, $w = 2$, $d = 1$; $(O_3) = 2.2$ mm, $g = 0.5$, and $i = 2$.

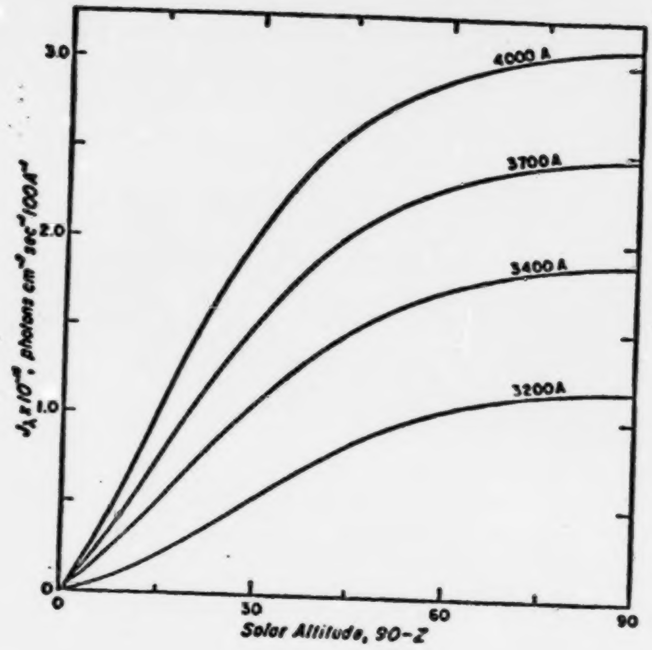

Figure 3-9. VARIATION IN ACTINIC IRRADIANCE WITH SOLAR ALTITUDE.

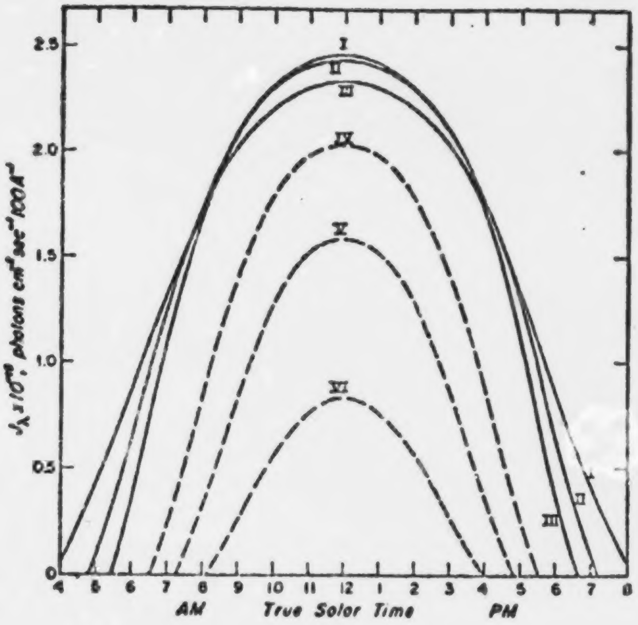

Figure 3-10. DIRUNAL VARIATIONS IN ACTINIC IRRADIANCE.

NOTE: Values illustrated are for the 100A interval of the solar spectrum centered at 3700A. The designations of the individual curves: I, 20° N lat, summer solstice; II, 35° N lat, summer solstice; III, 50° N lat, summer solstice; IV, 20° N lat, winter solstice; V, 35° N lat, winter solstice; and VI, 50° N lat, winter solstice.

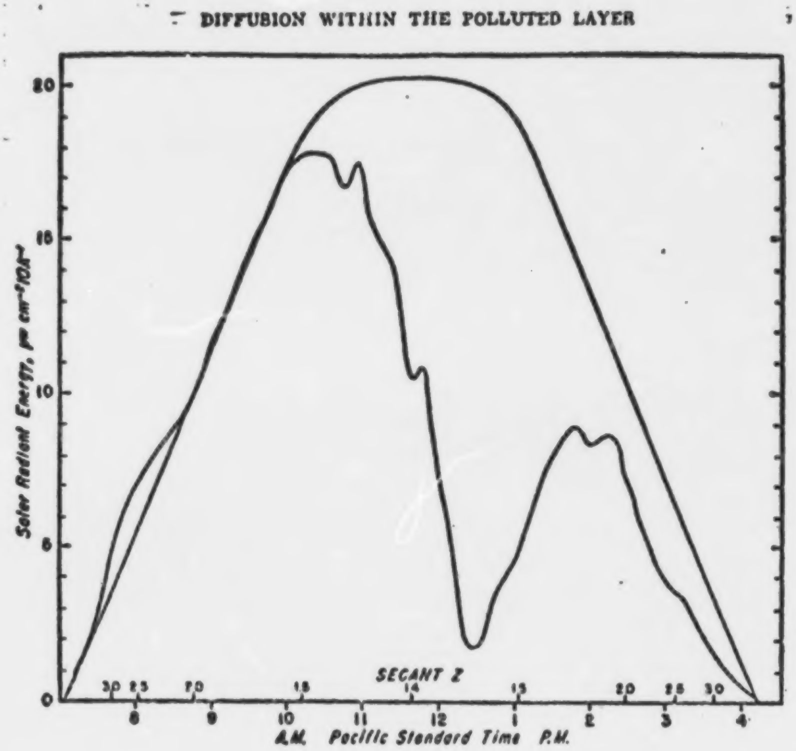

Figure 3-11. ATTENUATION OF DIRECT SOLAR ENERGY BY PHOTOCHEMICAL SMOG.

NOTE: Both lines represent the direct solar energy over a 10A bandwidth centered at 3235 A, incident on a normal surface at 800 feet elevation. The smooth line is $I_{o\lambda}Ts_{\lambda}Ta_{\lambda}$, calculated from Table 1 and equations (11-9), (II-11) and (II-13) with P=985 mb, w-2, d-0.5, and (Os)-2. The irregular line is the observed energy, from Stair's data for October 18, 1954 at Pasadena[21].

36 II. SOLAR RADIATION AND ITS ABSORPTION

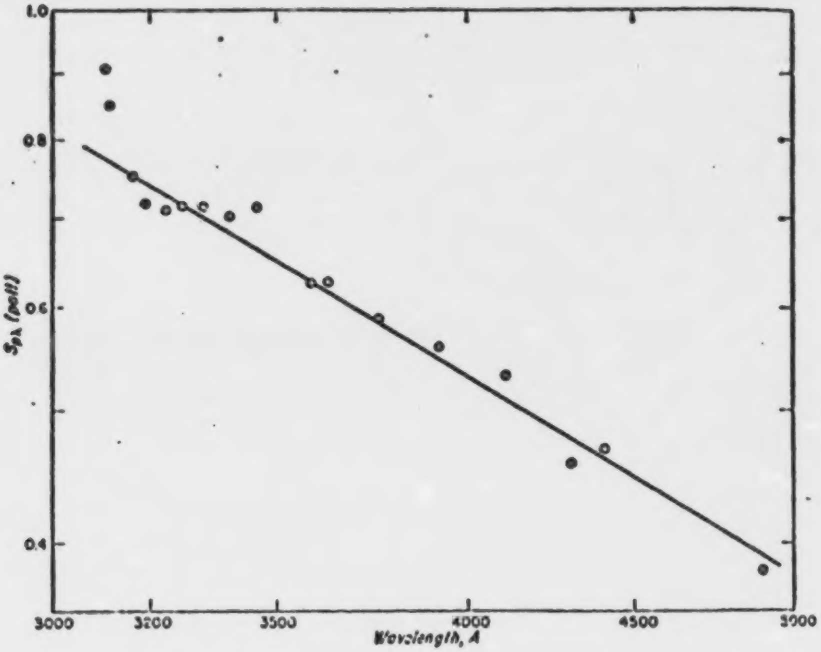

Figure 3-12. VARIATION IN THE ATTENUATION COEFFICIENT OF PHOTOCHEMICAL SMOG WITH WAVELENGTH.

Similar measurements were made in Los Angeles during October, 1965[19] with a variety of UV sensors, including a filter phototube, filter photocell, photochemical sensors, photosensitive plastic, and photochromic glass. Overall attenuation from smog in the region of 3000 to 3800 A incidental radiation was about 14 percent. Peak attenuation of 58 percent during the study period occurred during moderate to heavy smog as determined by chemical pollutant measurements.

Although the direct radiation from the solar beam may be reduced at some wavelengths by more than 80 percent as shown in Figure 3-11, the effect of smog on actinic irradiance is more difficult to estimate. The angular distribution of the scattered light is not known, but is likely to have a substantial effect on estimated values. Leighton[19], however, studied estimates based on two postulates which were intended to bracket the probable conditions. He concluded that for a solar zenith angle less than 60° (i.e., solar altitude above 30°), the average actinic irradiance in smog should be greater--by perhaps as much as 25 percent--than that found in the absence of smog. Since smog is more likely to be encountered when the solar zenith angle is low, this conclusion suggests that the generation of smog aerosols by the photochemical reaction system may further accelerate the photochemical process by increasing the actinic irradiance within the smog layer.

Nader and White[20], during a comparison study of horizontal plate and volumetric photovoltair sensors, did find some evidence of a slight increase in UV radiation in smoggy air as compared to clear air at solar zenith angles. Much more information from field measurements of UV radiation will be required to enable refined predictions of the effect of this parameter on photochemical smog formation.

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CHAPTER 4

ATMOSPHERIC REACTIONS

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A. INTRODUCTION

Reactions involved in the urban photochemical system fall readily into two classes: (1) primary photochemical reactions, in which contaminants, energized by light, rearrange or decompose to produce excited molecules or decomposition products; and (2) secondary reactions, in which products of the primary photochemical reactions react with other molecules, either contaminants or normal atmospheric constituents.

Photochemical reactions are initiated by the absorption of light by molecules. This interaction changes the configuration of electrons in a molecule, placing it in an electronically excited state. The short-lived excited molecule can lose its excess energy by collision with other molecules or by spontaneous emissions of energy, thereby returning to its original ground state. It may undergo internal rearrangement, may split up into two or more fragments, or may react with other molecules. Dissociation and rearrangement constitute photochemical primary reactions, whereas fluorescence and collisional deactivation do not lead to further chemical reaction. Thus, ordinarily, only a fraction of the light absorbed is effective in promoting chemical change.

Products of the primary processes are available to react further by entering into thermal (i.e., nonphotochemical) interactions with species with which they collide. Some important photochemical reactions involve the dissociation of excited molecules into free radicals* or atoms which, reacting with the components of polluted air, are responsible for most of the unique characteristics of photochemical smog

The secondary chemical reactions in urban atmospheres include atom-molecule, radical-molecule, radical-radical, and molecule-molecule reactions. The purpose of this chapter is to describe the processes of photochemical excitation and the subsequent types of reactions which it initiates.

B. PRINCIPLES OF PHOTOCHEMICAL PRIMARY REACTIONS

1. The Initiation of Photochemical Reactions by the Absorption of Solar Radiation

a. Light and Quanta

Light as a form of electromagnetic radiation is commonly described in terms of wave-like properties, especially the wavelength,**

$$\lambda = \frac{C}{\nu} \qquad (4\text{-}1)$$

in which C is the speed of light, 2.9979 x 10^{10} cm/sec., λ is its wavelength and ν is the frequency of the wave. However, certain properties of light, such as the photoelectric effect, require a particle theory. For the purposes of photochemistry, both theories are useful. In describing the absorption of energy, it is convenient to recognize the particle of light, or photon, as an irreducible bundle of energy, also called a quantum. The energy of a quantum is given by

---

*A radical is a group of atoms forming a coherent structure which may be part of various molecules; a free radical is a molecular fragment consisting of such a group, unattached to other groups or atoms, and carrying one or more unpaired electrons which render it very reactive chemically, as illustrated in this chapter. Free atoms, such as those of oxygen, are also very reactive for the same reason.

**The wavelength of a wave is defined as the distance between two successive peaks in that wave.

$$E = h\nu = \frac{hC}{\lambda} \tag{4-2}$$

in which h is Planck's constant, equal to 6.6256×10^{-27} erg-sec/quantum.

Light is emitted or absorbed by molecules in a quantum process that results in the transition of an electron from one quantum state to another. When light is absorbed, the electron is promoted to a higher energy level and when light is emitted, the electron falls to a lower energy level. The difference in energy between the two states is the same as the energy, $h\nu$, of the quantum (photon). (In photochemical notation, the term $h\nu$ is commonly used in place of a chemical symbol to represent a photon.)

The energy of interest in photochemical processes is that necessary to excite molecules and dissociate chemical bonds. Since most bonds are at least 40 Kcal/mole or greater in energy, the wavelengths of interest here are less than 7000Å, which corresponds to energies of 40 Kcal/mole or more. Solar radiation at the earth's surface between 3000Å and 7000Å is in the range that could excite molecules with sufficient energy to cause photochemical reactions. The scientific relation between available chemical energy and wavelength of absorbed light, derived from equation (4-2), is

$$E = 2.86 \times 10^5/\lambda \qquad (4\text{-}3)$$

where E is in Kcal/mole and λ in Angstroms. Table 4-1 shows the characteristics of various wavelength regions of the electromagnetic spectrum, named according to common usage. Some useful energy units, their relationships and the values of constants referred to in this chapter are given in Table 4-2.

b. The Laws of Photochemistry

Grotthuss (1817) and Draper (1843) stated that "Only the light which is absorbed by a molecule can be effective in producing photochemical change in the molecule." This statement constitutes the first law of photochemistry. The second law, described by Stark (1908-12) and Einstein (1912-13), states that each molecule taking part in a photochemical reaction absorbs precisely one quantum of the radiation which causes the reaction.

In the light of these laws, a useful concept for quantitative photochemistry is the quantum yield, which is the ratio between the extent of a particular reaction or the amount of a particular reaction product observed and the amount of light absorbed, in terms of molecules per quantum. Thus the second law implies that the quantum yield for excitation is unity, since every absorption event produces an excited molecule.

As another consequence, the sum of the primary process quantum yields is unity, since each excited molecule is soon converted either to a ground state molecule or to photochemical reaction products. These primary processes may include dissociation, rearrangement, fluorescence and any other

Table 4-1. APPROXIMATE LIMITS OF SPECTRAL REGIONS.

	Wavelength (a)	Frequency (c)	Wave number (d)	Energy (e)
	A (b)	cycles/sec	cm^{-1}	kcal/mole
Far ultraviolet	below 3000	above $1x10^{15}$	above $3x10^{4}$	above 95
Near ultraviolet	3000 to 4000	0.75 to $1(x10^{15})$	2.5 to $3(x10^{4})$	71 to 95
Visible	4000 to 7000	0.43 to $0.75(x10^{15})$	1.4 to $2.5(x10^{4})$	41 to 71
Near infrared	7000 to 30,000	0.10 to $0.43(x10^{15})$	0.3 to $1.4(x10^{4})$	10 to 41
Far infrared	above 30,000	below $0.43x10^{15}$	below $0.3x10^{4}$	below 10

(a) Wavelength, usually denoted by $\underline{\lambda}$, is defined as the distance between crests of a wave.

(b) 1 Ångstrom, abbreviated $\underline{\mathring{A}}$ or $\underline{A}$, is 10^{-8} centimeter.

(c) Frequency, usually denoted by $\underline{\nu}$, is the number of wave crests passing a point in a given time.

(d) Wave number, $\underline{\bar{\nu}}$, is the reciprocal of the wavelength (i.e., $\bar{\nu} = 1/\lambda$).

(e) Energy available for chemical transformations or excitation of atoms or molecules absorbing light.

Table 4-2. SOME USEFUL UNITS AND CONVERSION FACTORS.

	erg/molecule	e.v	cm^{-1}	cal/mole
erg/molecule	1	6.242×10^{11}	5.036×10^{15}	1.439×10^{16}
e.v.	1.602×10^{-12}	1	8.067	23,060
cm^{-1}	1.986×10^{-16}	1.2396×10^{-4}	1	2.858
cal/mole	6.949×10^{-17}	4.338×10^{-5}	0.3499	1

1 erg = 2.39×10^{-8} calories.

processes that lead to the deactivation or change in the molecule that has absorbed the quantum of energy. Whatever the process, only one quantum of energy has been absorbed by each molecule. Therefore, the quantum yield for a primary process can reach a maximum of one if every absorption event results in that process. The quantum yield for primary photochemical reaction is less than one if some of the molecules that are excited are subsequently deactivated and restored to their original states.

On the other hand, any values of observed over-all quantum yields greater than unity indicate the existence of secondary (thermal) reactions. This means that, following the primary processes, thermal reactions involving the products of these processes destroy more of the original molecules. Thus, more molecules are lost than quanta of light absorbed. Detailed examples are given in the following sections.

The Beer-Lambert law is also applicable to the systems encountered in photochemical smog. The magnitude of the absorption coefficient serves as an index of the relative amount of absorption to be expected at a given wavelength of light. If the absorption coefficient of a given species is appreciable in the range of 3000Å to 7000Å, that species will be an important absorber of sunlight and, therefore, must be considered in the discussion of the primary processes in atmospheric photochemistry. Nonabsorbers, however, may be important in subsequent thermal reactions.

c. Photochemical Primary Processes for Simple Molecules

The energy possessed by atoms and molecules may be considered to take on various forms. In atoms, the energy can be nuclear or electronic, while in molecules consisting of more than one atom the energy can be nuclear, electronic, rotational or vibrational, corresponding to the various modes of energy absorption. Translational or kinetic energy of motion is common to all molecules.

The absorption of electromagnetic radiation may excite any of these modes of activity if the radiation is of the proper wavelength. Quantum theory asserts that the energy can be absorbed or emitted only in discrete packets called quanta.

Each time a quantum of energy of a given kind of absorbed, an increment of activity of the appropriate kind is stimulated. Thus, when energy corresponding to wavelengths of about 10^8 Å is absorbed, a molecule will rotate more energetically. When energy corresponding to 10^4 Å is absorbed, the molecule will also vibrate more energetically. When energy corresponding to wavelengths less than 7×10^3 Å is absorbed, an electronic change is induced in the molecule. These changes to higher energy take place in single quantum jumps and the molecules are said to be raised to higher quantum states or energy levels. In the photochemical process, only those absorptions that cause electronic change lead to photochemical activity.

A number of excited states are usually available for various values of the excess electronic energy for a particular type of molecule. When it is necessary to differentiate between these states, they are referred to by quantum mechanical designations known as "term symbols." For example, the ground state of the oxygen molecule is $^3\Sigma_g^-$, its first excited state is $^1\Delta_g$, and its second excited state is ${}^1\Sigma_g^+$. The ground state of the oxygen atom is ${}^3P$, while the lowest excited state is ${}^1D$. Detailed explanations of these terms can be found in standard texts on quantum chemistry.

For convenience, less specific indications of electronic excited states are often used; thus, $O_2\ ({}^1\Delta_g)$ is often referred to simply as "singlet oxygen" in contrast to the triplet ground state, ${}^3\Sigma_g^-$. Again, the asterisk is often applied to indicate an unspecified excited state; for example, O_2^* might stand for any of the excited states of molecular oxygen, without discriminating between them.

Processes in which molecules are changed from one electronic state to another by absorption or emission of energy are called transitions and often written in a manner analogous to chemical reactions. Thus

$$O_2({}^3\Sigma_g^-) + h\nu \rightarrow O_2({}^1\Sigma_g^+) \tag{4-4}$$

represents the transition of oxygen from the ground state to the second excited state of an oxygen molecule, caused by absorption of a photon. (Light appropriate for this transition is in the wavelength range from 6920Å to 7660Å.)

A description of all the possible energy states of any given molecule and of the processes which may give rise to the various transitions among them constitutes a very complicated exercise in theoretical photochemistry, for which the reader is referred to standard texts. For an approximate understanding of the photochemistry of urban atmospheres, it is sufficient to recognize the following general considerations:

1. An electronically excited molecule is produced whenever a molecule absorbs a photon.

$$AB + h\nu \rightarrow AB^* \qquad \text{(excitation)} \qquad (4\text{-}5)$$

2. The lifetime of the excited molecule is short, and can be terminated by various processes: decomposition (4-6), reaction (4-7), fluorescence (4-8), collisional deactivation (4-9).

$$AB^* \rightarrow A + B \qquad \text{(dissociation)} \qquad (4\text{-}6)$$

$$AB^* + C \rightarrow \text{Products} \qquad (4\text{-}7)$$

$$AB^* \rightarrow AB + h\nu \qquad \text{(fluorescence)} \qquad (4\text{-}8)$$

$$AB^* + M \rightarrow AB + M \qquad \text{(collisional deactivation)} \qquad (4\text{-}9)$$

Some of these processes lead to disappearance of the original molecule and formation of photochemical products, while others do not.

3. Decomposition of the excited molecule is very rare unless the quantum energy of the absorbed photon exceeds the bond energy of at least one chemical bond in the molecule.

4. Energy can be transferred from the excited molecule to another molecule with which it collides. The latter molecule then

behaves as if it had absorbed light, while the original absorbing molecule is deactivated. (This process is called photosensitization. It seems to be rather rare in the urban atmosphere, but may be responsible for some production of singlet oxygen.)

The processes described in equation (4-5) followed by (4-6) or (4-7) constitute possible photochemical primary reaction paths, while those described by (4-5) followed by (4-8) or (4-9) return the molecule to its original state and do not lead to chemical change.

2. Molecules that Absorb Light in Urban Atmospheres

A very large number of compounds absorb some sunlight in the atmosphere. However, the absorption will not promote photochemical reactions if the energy is too low, nor will the reaction be of importance if the intensity is too low. The energies necessary to dissociate certain types of chemical bonds are listed in Table 4-3. An expression derived from the Beer-Lambert law is

$$I_a = I_o(1-10^{-\alpha cl}) \tag{4-10}$$

where I_o is the intensity of incident light, α is the decadic absorption coefficient* of the absorber, c is its concentration, and l is the length of the absorption path. Since the absorption coefficient is a function of wavelength, to obtain total absorption values, equation (4-10) must be applied for all the wavelengths absorbed, and the values of I_a summed (or integrated) over the range of interest.

Absorption rates for most of these compounds in urban atmospheres were estimated and presented by Leighton[1] as a function of solar zenith angle (Figure 4-1). All indications are that nitrogen dioxide is the dominant absorber in terms of specific rates.

A summary of the molecules of interest in "smog" with their absorption coefficient ranges and wavelengths is given in Table 4-4.

Most of the molecules shown in Table 4-4 absorb light over a very limited range within the 3000Å to 7000Å region of the spectrum. Absorption is limited to a region near 3000Å where the intensity in sunlight is low because of absorption in the upper atmosphere. In addition, most of their absorption coefficients are quite low. As a consequence, these molecules are not considered important as principal absorbers in urban atmospheres.

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*The notation used here is that of Leighton.[1] It is to be noted that some authorities[2] call this coefficient the "extinction coefficient" and denote it by ε.

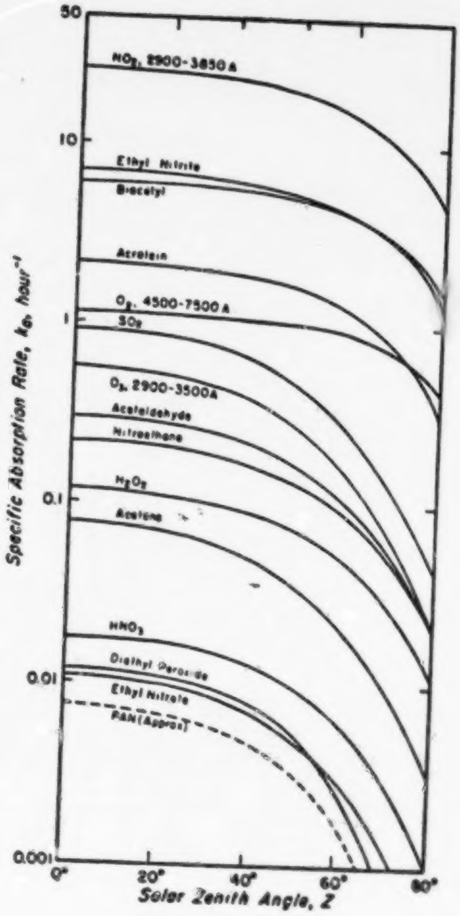
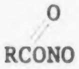
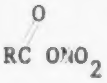


Figure 4-1. SUMMARY OF SPECIFIC ABSORPTION RATES.

Table 4-3. SOME BOND ENERGIES OF MOLECULES OF INTEREST IN PHOTOCHEMICAL SMOG.

Molecule	Bond	Energy Kcal/mole
O_2	O-O	118.3
O_3	O_2-O	25.2-26
CO	C-O	257
CO_2	OC-O	127
NO	N-O	151
NO_2	ON-O	72.7
SO_2	OS-O	131
H_2O	H-OH	119
HO	H-O	102
HO_2	H-O_2	47
H_2	H-H	104.2
HCO	H-CO	18
RCHO	R-CHO	80
CH_3COCH_3	$CH_3C^{=O}-CH_3$	79
HNO	ON-H	49
HONO	ONO-H	78
$HONO_2$	O_2N-OH	53
RONO	RO-NO	36-40
RONO	R-ONO	55-60
$RONO_2$	RO-NO_2	36-37
$RONO_2$	R-ONO_2	78-79

Table 4-4. SPECIES THAT ABSORB SUNLIGHT IN THE REGION 3000Å to 7000Å.

Substance	Maximum Absorption Coefficients (liter mole^{-1} cm^{-1}	Wavelength of Maximum Absorptions within Range (Angstroms)
O_2	7×10^{-6}	6900
O_3	110	3000
NO_2	171	4000
SO_2	220	3000
	121	3000
HNO_3 ($HONO_2$)	1.2	3000
$RONO_2$	0.9	3000
RONO	40	3600
$RONO_2$	8.4	3000
	5	3000
RCHO	16	3000
RCOR'	12	3000
ROOR'	2.3	3000
 $R\overset{\overset{O}{/\!/}}{C}ONO$	--	--
 $R\overset{\overset{O}{/\!/}}{C}\,ONO_2$	--	--
PAN	0.5	3000

Ozone and sulphur dioxide do have appreciable absorption coefficients in the range of interest, but their main absorption is near 3000Å where little sunlight energy is available. Absorption by ozone is of sufficient energy to dissociate the molecules and some photodissociation should take place. However, in the case of SO_2, even if absorption does take place, the energy at 3000Å is not sufficient to cause the molecule to dissociate (the bond energy of OS-O is about 131 Kcal/mole). The absorption spectrum of SO_2 is shown in Figure 4-2.

Figure 4-3 shows the absorption spectrum of NO_2 from 2500Å to 5000Å. It can be seen that absorption takes place over the entire range. In addition, it has been shown that photodissociation is possible below 4350Å. It is evident, therefore, that NO_2 is the principal absorber of sunlight, and plays one of the most important roles in the photochemical process that takes place in the urban air. Its photodissociation yields free oxygen atoms that react further with hydrocarbons and other components of polluted air. As discussed below, the subsequent molecular and free radical reactions can explain a great deal of the smog process.

Although some of the products of photochemical and thermal reactions may be formed in appreciable quantities, their residual concentrations in the air may be limited by photodissociation. This is more likely for those with large absorption coefficients (Table 4-4), since they would absorb sunlight more strongly. NO_2 is an example of this type of behavior.

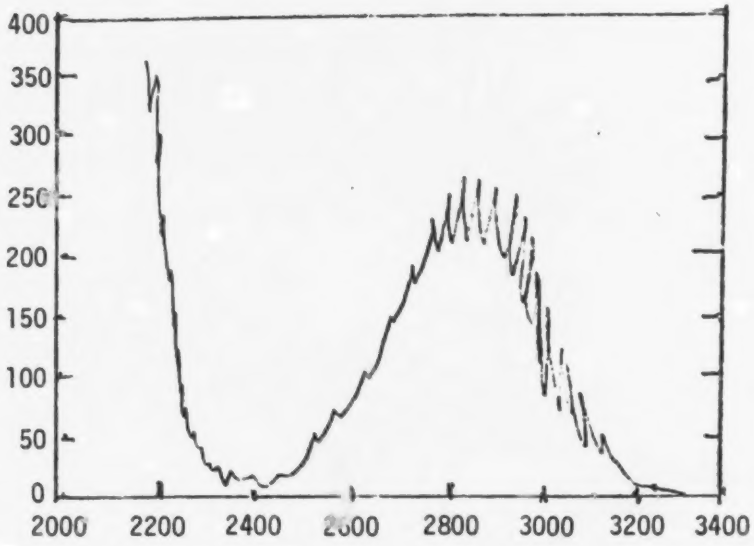


Figure 4-2. ABSORPTION SPECTRUM OF SO_2 (g) AT 25° C.

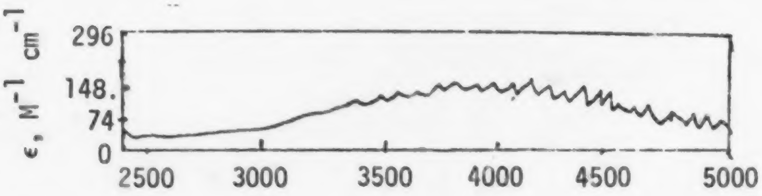


Figure 4-3. ABSORPTION SPECTRUM OF NO_2 AT 25° C.

3. Photochemical Primary Processes for Absorbers in Urban Atmospheres

a. Oxygen

The absorption by ordinary molecular oxygen ($^3\Sigma_g^-$) is in general too weak to lead to dissociation. Absorption between 6870Å and 6920Å yields about 41.5 Kcal/mole. The energy required for dissociation is about 119 Kcal/mole. Therefore, the direct dissociation of O_2 is negligible. However, oxygen may be excited by the spin-forbidden process,

$$O_2\ (^3\Sigma_g^-) + h\nu \rightarrow O_2\ (^1\Sigma_g^+) \qquad (4\text{-}11)$$

The excited ($^1\Sigma_g^+$) molecules might react directly with ozone or other species.

A new photo-oxidation mechanism based on singlet molecular oxygen has been proposed by Pitts and coworkers.[4,5] Singlet molecular oxygen has a theoretical lifetime of only a few seconds, thus the concentrations produced by direct absorption of sunlight can be expected to be quite small. This led Leighton[1] to conclude in 1961 that the role of O_2* was unimportant. Pitts, et al.[4,5] pointed out that a high yield of singlet oxygen might be obtained in a system in which an organic molecule absorbs energy from solar radiation and then, on collision, transmits it to normal molecular oxygen to produce singlet excited oxygen. The overall mechanism is represented as

$$D(S_o)+h\nu = D^*(S_1)$$

$$D^*(S_1) = D^{**}(T_1)$$

$$D^{**}(T_1) + O_2(^3\Sigma_g^-) = D(S_o) + O_2(^1\Sigma_g \text{ or } ^1\Delta_g^+)$$

(where D represents the "donor" organic molecule). Subsequent reaction of $^1O_2$ with olefinic substances produces thermally unstable hydroperoxides which may be involved in the rapid conversion of NO to NO_2.

b. Ozone

The photolytic processes that are energetically possible[6] are given in Table 4-5.

Table 4-5. SPECIES ENERGETICALLY POSSIBLE FROM $O_3 + h\nu \rightarrow$.

Limiting Wavelength	Species
11,400	$O_2(^3\Sigma_g^-) + O(^3P)$
5,900	$O_2(^1\Delta_g) + O(^3P)$
4,600	$O_2(^1\Sigma_g^+) + O(^3P)$
4,100	$O_2(^3\Sigma_g^-) + O(^1D)$
3,100	$O_2(^1\Delta_g) + O(^1D)$

Most of these processes are spectroscopically forbidden and, therefore, do not occur at appreciable rates. However, the O atoms and the excited O_2 molecules, to the extent that they are produced, would presumably contribute to secondary reactions in urban atmospheres.

c. Nitrogen Dioxide

Nitrogen dioxide is probably the most important absorber. At wavelengths below 4047Å, it dissociates readily[7] by the process,

$$NO_2 + h\nu \rightarrow NO + O(^3P) \qquad (4\text{-}12)$$

The oxygen atoms produced in this reaction are probably responsible, directly or indirectly, for the majority of the thermal oxidation reactions in urban photochemistry. The primary process probably involves direct excitation from $^2A_1$ (the ground state for NO_2 to $^2A_2$ for energies greater than the ON- bond energy of 71.8 Kcal/mole. However, at 4047Å the molecule could be excited to the $^2B_2$ state and then cross over into the $^2A_1$ state and hence dissociate according to equation (4-12).

d. Sulfur Dioxide

The energy required for dissociation into SO and O is about [illegible] Kcal/ mole corresponding to a wavelength of about 2180Å. This energy is not available in urban atmospheres. Sulfur dioxide may be excited by sunlight in the region of 3200Å and lower wavelengths (Figure 4-2).

$$SO_2 + h\nu \rightarrow SO_2^* \qquad (4\text{-}13)$$

The first excited state may be a triplet[8] with a lifetime of 1.3 x 10^{-2} to 2.2 x 10^{-3} seconds. It is estimated that the natural radiative lifetime would be about 2 x 10^{-7} seconds if the molecule were in a singlet state as a result of irradiation in the region of 3000Å to 3200Å.

The natural lifetime, or mean radiative lifetime, of an electronically excited species is the average time in seconds that the excited species retains its excess energy in the absence of collisional deactivation. The mean lifetime is equal to the inverse of the rate constant for the process by which the molecule loses its energy by radiation (i.e., fluorescence, phosphorescence, etc.). When a molecule has a relatively long lifetime, say

$> 10^{-5}$ seconds, it is an indication that it is in an electronic state from which it is forbidden, spectroscopically, to fall into the ground state by radiation. The triplet state meets these conditions, whereas molecules in the singlet state may radiate back to ground state readily and have lifetimes shorter than 10^{-7} seconds. The excited SO_2* may be able to react directly with components of smog such as hydrocarbons.[9]

e. Nitric Acid

Although Reynolds and Taylor[10] observed the formation of NO_2 corresponding to the reaction in sunlight, the absorption spectrum of HNO_3 indicates very weak absorption in the region above 3000Å.

$$HNO_3 + h\nu \rightarrow OH + NO_2 (-53\ \text{Kcal}) \tag{4-14}$$

However, Jaffe and Ford[11] have shown that HNO_3 will yield NO_2 in the presence of NO_2 and light. Since a trace of NO_2 will stimulate the reaction, equation (4-14) probably results from

$$O + HNO_3 \rightarrow OH + NO_3 \tag{4-15}$$

with subsequent formation of NO_2. The O atoms derive from the photolysis of NO_2 as in equation (4-12).

f. Alkyl Nitrates

The photolysis of ethyl nitrate at 3130Å serves as an example of the alkyl nitrate primary process. The most probable photodissociation mode is

$$RCH_2ONO_2 + h\nu \rightarrow RCH_2O + NO_2 \tag{4-16}$$

g. Alkyl Nitrites

The most generally accepted process for RONO is

$$RONO + h\nu \rightarrow RO + NO \qquad (4\text{-}17)$$

Subsequent reactions of the RO radical are probably important in these systems. Some results with tert-butyl nitrite and tert-pentyl nitrite have given quantum yields, $\phi_{17} = 1.0$. This is strong support for process (4-17) as compared with other possibilities such as

$$RCH_2ONO + h\nu \rightarrow RCHO + HNO \qquad (4\text{-}18)$$

or

$$RCH_2ONO + h\nu \rightarrow RCHO + NOH \qquad (4\text{-}19)$$

h. Nitroalkanes

The only well-established primary process is the formation of the alkyl radical and NO_2 according to the reaction:

$$RNO_2 + h\nu \rightarrow R + NO_2 \qquad (4\text{-}20)$$

For nitromethane[12,13,14,15] it was shown that

$$CH_3NO_2 + h\nu \rightarrow CH_3 + NO_2 \qquad (4\text{-}21)$$

was more important than

$$CH_3NO_2 + h\nu \rightarrow CH_2O + NOH \qquad (4\text{-}22)$$

$$\phi_{22} >> 0.04$$

For nitroethane, in addition to process (4-20), a second reaction,

$$CH_3CH_2NO_2 + h\nu \rightarrow CH_2{=}CH_2 + HONO \qquad (4\text{-}23)$$

was important. ($\phi_{23} \approx 0.08$ at 3130Å.) These data indicate that nitro compounds first formed in thermal reactions could photolyze further and be destroyed so that no appreciable concentration is found in polluted air.

i. Aldehydes

Photodissociation of aldehydes is only possible energetically at wavelengths of about 3400Å and shorter. The principal dissociation reaction is

$$RCHO + h\nu \rightarrow R + HCO \tag{4-24}$$

At shorter wavelengths,

$$RCHO + h\nu \rightarrow RH + CO \tag{4-25}$$

is possible. However, at 3130Å, $\phi_{25}/\phi_{24} = 0.001 - 0.05$, indicating that the only reaction for consideration here is (4-24). These conclusions have been verified for simple aliphatic aldehydes such as formaldehyde, acetaldehyde, propionaldehyde, etc.[2]

j. Ketones

When alkyl ketones are photolyzed,

$$RCOR' + h\nu \rightarrow RCO + R' \tag{4-26}$$

$$\rightarrow RR' + CO \tag{4-27}$$

at 3130Å, equation (4-26) is favored, process (4-27) increasing at lower wavelengths. Therefore, (4-26) should be the only important photodissociation mode in urban atmospheres.

k. Peroxides

Alkyl peroxides absorb weakly in the range of 3000Å to 7000Å. The process[2] most consistent with observation is

$$ROOR' + h\nu \rightarrow RO^* + R'O^* \tag{4-28}$$

The radicals are quite energetic even at 3130Å, where they carry off about

56 Kcal/mole. Subsequent fragmentation of the radicals is to be expected.

l. Acyl Nitrites, Nitrates, and Peroxynitrates

There is no experimental evidence of the primary photochemical processes that may take place with acyl nitrites, R(CO)ONO, acyl nitrates, $R(CO)ONO_2$ or peroxyacylnitrates, $R(CO)OONO_2$. Leighton[1] has speculated on possible photochemical reactions and the reader is referred to his book for further possible applications of these compounds to smog.

m. Particulate Matter

Particulate matter such as metal oxides, i.e., ZnO, can absorb light and give rise to photosensitized surface reactions. For example, with zinc oxide-water-sodium formate systems, a reaction produces H_2O_2 with a quantum yield of 0.5[16] at 3130Å. Since the urban atmospheres contain particles of metallic oxides such as PbO and Pb_3O_4, particulate photosensitized reactions might be of some importance.

For a more complete discussion of photochemical primary processes the reader may refer to Calvert and Pitts' excellent text[2] "Photochemistry," from which most of the information cited above was obtained.

C. ATMOSPHERIC REACTIONS

1. Kinetics of Thermal and Free Radical Reactions

Reactions that involve products of the primary photochemical processes (described in paragraph B above) are called secondary reactions. These include the interactions of the products of photodissociation with each other and with any other species in polluted air. The reactions that result from the collisions of various chemical species (not including light) are referred to as thermal reactions. These include the interactions of normal molecules as well as the interactions of free radicals with molecules or with themselves.

In some circumstances, small numbers of free radicals can induce a very large number of reactions; they are therefore important in atmospheric photochemistry. Free radicals in polluted air arise mainly from the dissociation of excited molecules that have absorbed solar radiation (see paragraph B above) or from reactions of such radicals with ordinary molecules. Free atoms and free radicals are very reactive species because they have unsatisfied bonding orbitals. That is, they have unpaired electrons that normally would interact with other unpaired electrons and nuclei to form strong chemical bonds. Upon collision with molecules and other atoms or free radicals, new stable molecules and new free radicals can be formed. Thus, when free radicals are formed in polluted air, they may rapidly initiate a chain of reactions that subsequently lead to the formation of the many species found after irradiation.

A brief introduction to the principles of chemical kinetics is presented in the following paragraphs in order to facilitate the understanding of air pollution systems. The presentation consists of definitions and empirical relationships and some theories that help to explain the observed phenomena. The concept of rates of reactions and rate constants is especially helpful in judging the relative importance of competing processes in photochemical smog.

a. Rate Laws

It has been found experimentally that the rates of simple chemical reactions are a function of the concentrations of the reacting species,

$$\text{Rate} = k(A)^n(B)^m \qquad (4\text{-}29)$$

in which the rate may represent the amount of reactant being lost per unit time per unit volume or the amount of products being formed per unit time per unit volume. The units of rate may, for example, be moles per liter per minute. $\underline{k}$ is called the specific rate constant and is the rate at unit concentration of reactants. Some useful units and conversion factors[1] for concentrations and rate constants are presented in Table 4-6.

(A), and (B), etc., are the concentrations of the reactants; the exponents, n and m, are small integers--0, 1 or 2. The over-all order of the reaction is equal to the sum of n, m, etc. Most elementary reactions are of order 2, although orders 1 and 3 are possible.

A complex chemical reaction takes place in a series of a simple elementary steps. Although these steps may not always be known, the investigator may postulate a reasonable set of elementary reactions in order to explain the appearance of products. Such a set of reactions is called a mechanism. From this set of simple reactions, one may derive a rate law and compare it with experimental observations. If reasonable agreement is shown, the postulated mechanism is a possible one. A test of this kind may be made on the postulated reactions that take place in polluted air. For each elementary reaction, one can write a rate expression. For example, for the process,

$$A + B \rightarrow C \qquad (4\text{-}30)$$

$$C + D \rightarrow E \qquad (4\text{-}31)$$

Table 4-6. CONVERSION FACTORS.[1]

(Based on concentration in ppm and pphm relative to air at 1 atm, 25°C.)

Concentrations

moles $l^{-1} \times 2.445 \times 10^{9}$ = pphm

moles $cc^{-1} \times 2.445 \times 10^{12}$ = pphm

pphm $\times 4.09 \times 10^{-10}$ = moles l^{-1}

pphm $\times 4.09 \times 10^{-13}$ = moles cc^{-1}

Rate constants, k

Bimolecular

$l\ mole^{-1} sec^{-1} \times 2.45 \times 10^{-6} = ppm^{-1} min^{-1}$

$cc\ mole^{-1} sec^{-1} \times 2.45 \times 10^{-9} = ppm^{-1} min^{-1}$

$l\ mole^{-1} sec^{-1} \times 1.47 \times 10^{-6} = pphm^{-1} hr^{-1}$

$cc\ mole^{-1} sec^{-1} \times 1.47 \times 10^{-9} = pphm^{-1} hr^{-1}$

Termolecular

$l^{2}\ Mole^{-2} sec^{-1} \times 1.005 \times 10^{-13} = ppm^{-2} min^{-1}$

$cc^{2} mole^{-2} sec^{-1} \times 1.005 \times 10^{-19} = ppm^{-2} min^{-1}$

$l^{2} mole^{-2} sec^{-1} \times 6.03 \times 10^{-16} = pphm^{-2} hr^{-1}$

$cc^{2} mole^{-2} sec^{-1} \times 6.03 \times 10^{-22} = pphm^{-2} hr^{-1}$

the rate of formation of E is

$$\frac{d(E)}{dt} = k_{31} (C) (D) \tag{4-32}$$

But C may be a reactive intermediate such as a free radical, whose rate of formation may be equalled by its rate of reaction. That is, as soon as a C radical is formed, it reacts with D to form E. In this case,

$$\frac{d(C)}{dt} = 0 = k_{30}(A) (B) - k_{31}(C) (D) \tag{4-33}$$

from which, under so-called "steady-state" conditions,

$$(C)_{Steady-State} = k_{30}(A) (B)/k_{31}(D) \tag{4-34}$$

Insertion of this result in (4-32) gives

$$\frac{d(E)}{dt} = \frac{k_{31}(D) k_{30}(A) (B)}{k_{31}(D)} = k_{30}(A) (B) \tag{4-35}$$

The derived rate law will verify that the mechanism (4-30) and (4-31) is appropriate if experiment shows that the rate of formation of E is directly proportional to the product of (A) times (B).

b. Collision Theory

The most frequent chemical reactions in the gas phase involve bimolecular interactions. In the simplified theory, the interaction is viewed as one of the collision between two hard spheres. When two spheres collide, they come together at a distance between centers called the collision diameter σ, as shown schematically in Figure 4-4. In this view, two molecules A and B cannot react unless they collide, but not all such collisions lead to reaction. At a given temperature, a fixed proportion of appropriate collisions

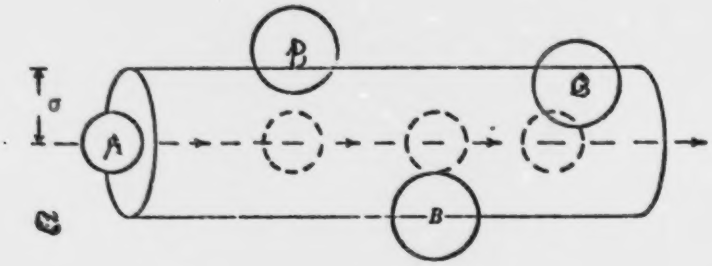


Figure 4-4. MOLECULES A AND B IN COLLISION.

result in reaction; this proportion is known as the collision yield and is exponentially related to the temperature as expressed in equation (4-36)

$$y = pe^{-E/RT} \tag{4-36}$$

where E is the activation energy of the reaction, R is the universal gas constant, T is the absolute temperature and p is a probability factor which is also characteristic of the reaction.

According to simple kinetic theory of gases, appropriate collisions occur at a rate proportional to the concentrations of the colliding molecules; thus

$$r_c = Z_{AB}(A)(B) \tag{4-37}$$

where r_c is the rate of collision (in a unit volume of the gas phase) and Z_{AB} is a frequency factor which can be estimated from the dimensions of the colliding molecules. The product of this collision rate by the collision yield y is the rate of reaction of A with B,

$$r_{A+B} = pZ_{AB}e^{-E/RT}(A)(B) \tag{4-38}$$

Comparison with equation (4-29) shows that, if m and n are both unity, the rate constant k can be identified as the product of the collision yield, y, by the frequency factor, Z_{AB}. Thus

$$k = pZ_{AB}e^{-E/RT} = yZ_{AB} \tag{4-39}$$

Values of Z_{AB} are normally of the order of magnitude of $3x10^{11}$ liter/mole sec., equivalent to about $4x10^{7}ppm^{-1}hr^{-1}$. Collision yields depend strongly on the energy of activation, but cannot be larger than unity. Values of k, for all practical purposes, are thus constrained to be smaller than $3x10^{11}$ liter/mole sec. Furthermore, the value of k is considered to be less than $3x10^{11}$ times the exponential factor, $e^{-E/RT}$; thus, if a lower limit for $\underline{E}$ can be reliably estimated, an upper limit less than $3x10^{11}$ liter/mole sec. can be assigned for $\underline{k}$. This procedure can be very useful in estimating rates of elementary steps for use in postulated mechanisms of complex reactions, as shown in Chapter 6 in connection with the photochemical smog reaction system.

In summary, a chemical reaction results when two molecules collide with sufficient energy and in the proper orientation to produce the activated complex. The collision theory offers, for any specified elementary reaction, a means of estimating an upper bound to its specific rate constant. As a general explanation of chemical rate phenomena, the collision theory has several weaknesses. First, the factor $\underline{p}$ may not be readily correlated with the structures and properties of the reacting molecules. Secondly, abnormally high rates cannot be interpreted on this basis. These faults can be overcome to a large extent by the application of absolute rate theory. (For a brief introduction to this more elaborate theory, refer to Calvert and Pitts (2, p. 608ff).

2. Thermal Reactions

As a result of the photodissociation processes, atoms, radicals and excited molecules are available to react thermally (that is, by collisions) with otherwise stable species. The list of these compounds includes nitrogen, water, carbon dioxide, carbon monoxide, nitric oxide, sulphur trioxide, sulphuric acid, alcohols, organic acids, and hydrocarbons, as well as compounds that do absorb sunlight (Table 4-4). All such interactions are classified as secondary reactions.

The most important secondary reactions include the conversion of NO to NO_2, the formation of ozone, and the oxidation of hydrocarbons. An extensive review of these reactions is presented in paragraph D. below. It is very useful to compare the rates of these reactions in order to ascertain which ones are more likely to predominate. If the rate constant is large and the concentrations of reactants are high, reaction proceeds rapidly. If the rate constants are too small or the concentrations of the reacting species are too low, reaction takes place slowly and is not important.

By way of illustration, one could compare the rates of the very important processes of olefin oxidation. The principal reactions are the oxidation by O atoms,

$$O + \rangle C{=}C\langle \rightarrow \text{Products}$$

and the oxidation by ozone

$$O_3 + \rangle C{=}C\langle \rightarrow \text{Products}$$

The range of specific rate constants for the oxygen atom reactions is about 10^8 to 10^{10} liter $mole^{-1}$ sec^{-1}, while those of ozone are from 10^3 to 10^4 liter $mole^{-1}$ sec^{-1}. These values apparently favor the oxygen atom reactions, since the ratio

$$\frac{k_O}{k_{O_3}} = 10^5 \text{ to } 10^7$$

However, the actual rates depend upon concentrations as well as rate constants, and the steady-state concentration of oxygen atoms relative to ozone is frequently about 10^{-4} to 10^{-6}. Using the rate laws,

$$\frac{\text{Rate}_{O}}{\text{Rate}_{O_3}} = \frac{k_O[O][\text{Olefin}]}{k_{O_3}[O_3][\text{Olefin}]}$$

Therefore, $\frac{\text{Rate}_O}{\text{Rate}_{O_3}} \approx 10$.

Under those conditions, oxygen atom oxidation of olefins might be only 10 times as fast as ozone reactions with the same olefins. Thus both oxygen atom and ozone oxidation could occur at appreciable rates, neither being negligible relative to the other. Such considerations are especially useful in comparing rates of competitive reactions, which are not uncommon in the development of photochemical air pollution.

3. The Generation of Free Radicals

Free radicals may be produced in photochemical smog in at least two important ways. In the first, a neutral molecule absorbs light and is promoted to an excited state. The excess energy in the molecule is eventually transferred into vibration of chemical bonds, and the molecule is split into two or more fragments which may be free radicals. Examples of free radicals produced in this manner by reactions discussed in paragraph B, above, are given in Table 4-7.

The second process of free radical formation involves the bimolecular reactions of molecules and radicals which produce excited intermediates which dissociate, producing new radicals. The reactions of O atoms, O_3 and NO_2 with hydrocarbons, especially olefins, give rise to this type of behavior.

Table 4-7. SOME FREE RADICALS AND ATOMS GENERATED BY PHOTOLYSIS

Absorber Molecules	Active Species Produced*	
O_3	O	oxygen atom
NO_2	O	oxygen atom
HNO_3	OH	hydroxyl
$RONO_2$	RO	alkoxyl
RONO	RO	alkoxyl
RNO_2	R	alkyl
RCHO	R + HCO	alkyl + formyl
RCOR	RCO + R	acyl + alkyl
ROOR	RO	alkoxyl

---

* R is any alkyl group.

The thermal dissociation of molecules is also possible. This process takes place when heat in excess of the bond energy is absorbed by a molecule as a result of energetic collisions. However, at ambient temperatures only a negligible fraction of molecules has sufficient energy to cause thermal dissociation.

Free radicals are also produced by the reaction of other free radicals with reactant molecules. Such reactions are discussed in paragraph 5 below, following the general introduction to chain reactions in paragraph 4.

Table 4-8 summarizes the kinds of free radicals that are probably formed by the action of sunlight on polluted air. It should be noted that NO, NO_2, NO_3 and even O_2 possess unpaired electrons and behave as free radicals in many instances. The general reactions of each of these are reviewed in paragraph D.

4. General Treatment of Radical Chain Reactions[17]

Free radical chain reactions are initiated by molecular collisions, photolysis or any other method that can generate free radicals. The first step can be represented by *

$$A \rightarrow mR + nB \qquad (4\text{-}40)$$

In one type of reaction chain, when the free radical chain carrier, R, collides with another molecule, it can continue the process by a propagation step such as

$$R + C \rightarrow R + D \qquad (4\text{-}41)$$

Here the radical R is reproduced so that it is free to repeat reaction (4-41) many times before the chain process is broken or terminated.

---

*A, B, D, C, and E are reactant or product molecules, and m and n are integers.

Table 4-8. FREE RADICAL CLASSES FORMED IN IRRADIATED POLLUTED AIR.

Name of Radical	Formula*
alkyl	$R\cdot$
alkoxyl	$RO\cdot$
peroxyalkyl	$ROO\cdot$
hydroxyl	$\dot{O}H$
hydroperoxyl	$HOO\cdot$
formyl	$H\dot{C}O$
acyl	$R\dot{C}O$
peroxyformyl	$H\overset{O}{\overset{/\!/}{C}}-OO\cdot$
peroxyacyl	$R\overset{O}{\overset{/\!/}{C}}-OO\cdot$
formate	$H\overset{O}{\overset{\|}{C}}O\cdot$
acylate	$R\overset{O}{\overset{\|}{C}}O\cdot$

---

*R is any alkyl group.

$$R + R + M \rightarrow R_2 + M \tag{4-42}$$

In reaction (4-42), two free radicals recombine to form a neutral molecule which cannot react further, thus breaking the chain.

An example of this kind of single-chain carrier process with second order breaking is the ortho-para hydrogen conversion,

initiation $$M + H_2(\text{o or p}) \rightarrow 2H + M \tag{4-43}$$

propagation $$H + H_2(\text{p}) \rightarrow H_2(\text{o}) + H \tag{4-44}$$

termination $$M + 2H \rightarrow H_2(\text{o or p}) + M \tag{4-45}$$

A more important case occurs with two chain carriers and second-order breaking,

initiation $$A \rightarrow R + S \tag{4-46}$$

propagation $$\left\{\begin{array}{ll} R + B \rightarrow S + C & \text{(4-47)} \\ S + D \rightarrow R + E & \text{(4-48)} \end{array}\right.$$

termination $$2R + M \rightarrow R_2 + M \tag{4-49}$$

Here R and S are two different free radical chain carriers.

A famous example of this kind of behavior is the formation of HBr from $H_2 + Br_2$

initiation $$Br_2 \rightarrow 2Br \tag{4-50}$$

propagation $$\left\{\begin{array}{ll} Br + H_2 \rightarrow HBr + H & \text{(4-51)} \\ H + Br_2 \rightarrow HBr + Br & \text{(4-52)} \\ H + HBr \rightarrow H_2 + Br & \text{(4-53)} \end{array}\right.$$

$$\underline{\text{termination}} \qquad 2Br \rightarrow Br_2 \tag{4-54}$$

Chain reactions of the kind that may occur in photochemical smog and involving free radicals like those in Table 4-8, are postulated in what is called the "Rice-Herzfeld[18] mechanism." The thermal or photochemical dissociation of acetaldehyde can be treated as follows,

$$\underline{\text{initiation}} \qquad CH_3CHO \rightarrow CH_3 + C\dot{H}O \tag{4-55}$$

$$CHO \rightarrow H + CO \tag{4-56}$$

$$\underline{\text{propagation}} \left\{ \begin{array}{ll} H + CH_3CHO \rightarrow H_2 + CH_3CO & (4\text{-}57) \\ CH_3 + CH_3CHO \rightarrow CH_4 + CH_3CO & (4\text{-}58) \\ CH_3CO \rightarrow CH_3 + CO & (4\text{-}59) \end{array} \right.$$

$$\underline{\text{termination}} \qquad 2CH_3 \rightarrow C_2H_6 \tag{4-60}$$

Using a steady-state approximation* on all free radicals, this mechanism leads to the rate expression

$$\text{Rate} = k_{58} \left(\frac{k_{59}}{k_{60}} \right)^{1/2} [CH_3CHO]^{3/2} \tag{4-61}$$

5. Free Radical Reaction Types in Photochemical Smog

The free radical types shown in Table 4-8 react with virtually all of the species in polluted air. The important reactions include those with O_2, NO, NO_2, O_3 and reactions among the free radicals themselves. A detailed description of these reactions is given in paragraph D. A few general features of these reactions, however, are of interest here.

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*The steady-state approximation is based on the assumption that the free radicals are produced and lost at the same rates so that the concentrations remain constant as long as reactants are available. This permits one to set $\frac{d[R]}{d[t]} = 0$ and solve for a steady-state concentration as was done in equation (4-33).

Oxygen molecules are the most abundant reactive species in air; however, most of the reactions of O_2 are relatively slow. Oxygen molecules can add to free radicals producing more complex radicals:

$$R\cdot + O_2 \rightarrow RO_2\cdot$$

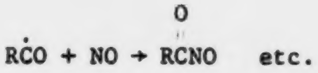
They can enter into metathetical reactions:

$$\dot{C}H_3 + O_2 \rightarrow CH_2O + H\dot{O}$$

Nitric oxide may add to free radicals quite readily, since it is itself an odd electron molecule.

$$R\cdot + NO \rightarrow RNO$$

or



$$R\dot{C}O + NO \rightarrow R\overset{O}{\overset{\|}{C}}NO \quad \text{etc.}$$

NO can be oxidized to NO_2:

$$RO\dot{O} + NO \rightarrow R\dot{O} + NO_2$$

Nitrogen dioxide may also add to free radicals, since it is an odd electron molecule.

$$RO\cdot + NO_2 \rightarrow RONO_2$$

It may also donate oxygen to some free radicals:

$$R\cdot + NO_2 \rightarrow RO\cdot + NO$$

and NO_2 may abstract hydrogen from free radicals:

$$RCH_2\dot{O} + NO_2 \rightarrow RCHO + HONO$$

Ozone may react directly:

$$R\cdot + O_3 \rightarrow RO\cdot + O_2$$

In addition, the zwitterions formed as a result of the attack of O_3 on olefins,

$$O_3 + R_2C{=}CR_2 \rightarrow R_2CO + R_2\overset{+}{C}O\overset{-}{O}$$

may react further to yield free radicals, although this has not been experimentally demonstrated.

Rates of these reactions depend on various factors determined in part by the structures of the substituent radicals. Details of individual reactions are discussed in paragraph D.

D. A THESAURUS OF PROPOSED REACTIONS IN THE URBAN PHOTOCHEMICAL SYSTEM

Experimental and theoretical research has produced considerable insight into the chemical reactions in photochemical smog. It is now widely accepted that the process involves photo-oxidation of hydrocarbon vapors, with NO_2 as the main effective primary absorber. However, detailed steps in the photo-oxidation are still subjects of conjecture. This paragraph presents a comprehensive collection of the chemical reactions which may be taking place in smog formation. The reactions are grouped by appropriate categories, e.g., inorganic reactions, free radical reactions, etc. A summary in each category cites the most probable reactions occurring in that category.

Photochemical smog reactions have been studied by a large number of investigators. Although references to original work are included where appropriate, no attempt has been made to cite all the references to studies of the chemistry of smog. In addition to this paragraph, the reader is referred to the reviews of Leighton,[19] Wayne,[20] Altshuller and Bufalini,[21] Stephens,[22] and Haagen-Smit and Wayne.[23]

1. Inorganic Reactions

A number of reactions can occur when air containing oxides of nitrogen is irradiated with sunlight in the absence of organic gases. The reactions which can occur are summarized in Table 4-9 and 4-10.

Table 4-9. INORGANIC REACTIONS.

$NO_2 + h\nu = NO + O$ (A1)

$O + O_2 + M = O_3 + M$ (A2)

$O_3 + NO = O_2 + NO_2$ (A3)

$O + NO_2 + M = NO_3 + M$ (A4)

$O + NO_2 = O_2 + NO$ (A5)

$O + O_3 = 2O_2$ (A6)

$O + NO + M = NO_2 + M$ (A7)

$O + O + M = O_2 + M$ (A8)

$NO_3 + NO = 2NO_2$ (A9)

$NO_3 + NO_2 = N_2O_5$ (A10)

$N_2O_5 = NO_3 + NO_2$ (A11)

$2NO + O_2 = 2NO_2$ (A12)

$NO_3 + NO_2 = NO + O_2 + NO_2$ (A13)

$NO_2 + O_3 = NO_3 + O_2$ (A14)

$O_3 + h\nu = O_2 + O$ (A15)

$2NO_3 = 2NO_2 + O_2$ (A16)

$NO + NO_2 + H_2O = 2HNO_2$ (A17)

$N_2O_5 + H_2O = 2HNO_3$ (A18)

$2NO_2 + H_2O = HNO_3 + HNO_2$ (A19)

$2HNO = N_2O + H_2O$ (A20)

$NO_3 + H_2O = HNO_3 + \dot{O}H$ (A21)

$H_2O + O = 2\dot{O}H$ (A22)

$O_2 + M = O + O + M$ (A23)

$O_3 + M = O + O_2 + M$ (A24)

$O_2 + O_2 = O + O_3$ (A25)

Table 4-10. RATE CONSTANTS FOR THERMAL HOMOGENEOUS INORGANIC REACTIONS.

Reaction Number	Rate Constant	Value* (ℓ, mole, sec.)	Reference
A2[a]	k_2	$1.68 \times 10^7 \exp(2.1/RT)$	24
A3	k_3	$1.17 \times 10^7 - 2.8 \times 10^7$ (300°K)‡	25
A4	k_4	10^{11} (300° K)	26
A5	k_5	3.3×10^9 (300°K)	27
A6	k_6	$1.205 \times 10^{10} \exp(-4.79/RT)$	24
A7	k_7	1.8×10^{10} (300°K) [or 7.5×10^8 ℓ/mole sec]	28
A8b	k_8	$1.379 \times 10^{12}\, T^{-1} \exp(-.34/RT)$	24
A9	k_9	5.6×10^9 (300°K)	29
A10	k_{10}	1.8×10^9 (300°K)	25
A11	k_{11}	0.24 (300°K)	25
A12	k_{12}	1.5×10^4 (300°K)	1
A13	k_{13}	2.5×10^5 (300°K)	25
A14	k_{14}	$2 \times 10^4 - 4.3 \times 10^4$ (300°K)	29,30,31
A16	k_{16}	1.2×10^4 (300°K)	25
A17	k_{17}	4.3×10^7 (300°K)	32
A23b	k_{23}	$2.75 \times 10^{16}\, T^{-1} \exp(-118.7/RT)$	24
A24a	k_{24}	$9.94 \times 10^{11} \exp(-22.72/RT)$	24
A25	k_{25}	$1.28 \times 10^{10} \exp(-100.6/RT)$	24

---

* Activation energies are in Kcal mole^{-1}

‡ Range of values represents reported variations

a. if M is O_3.

b. if M is O_2.

The main reactions which occur are (A1,A2,A3). The primary photolysis rate of (A1) was estimated by Leighton[19] to be 0.4 min^{-1} with bright sunlight at a zenith angle of 20 degrees. Reactions (A2) and (A3) are also very fast, resulting in a conversion of light to heat in the sequence, and the establishment of a steady-state.

Although (A1 to A3) are the most important inorganic reactions, several other reactions may be of secondary importance. Reactions (A4 to A8) involve reactions of oxygen atoms which must compete with (A2). Reaction (A4) may be important in systems in which the concentration of NO_2 is much higher than in polluted air. Reaction (A7) may be important when NO is in great excess. Reaction (A5) is too slow to compete with (A4). Reactions (A6) and (A8) are too slow to be of any importance.

Reactions (A9) to (A14) involve other reactions of O_3 and nitrogen oxides. The most important processes consuming NO_3 are (A9) and (A10). These two reactions are fast enough to prevent the accumulation of NO_3 from (A4). Of the two reactions (A9) is somewhat faster than (A10), preventing the accumulation of N_2O_5. Reaction (A11) is very slow and probably not competitive with (A18) when water vapor is present. Reaction (A12) accounts for the oxidation of NO to NO_2 in the dark but is far too slow to be of importance in sunlight. Reaction (A13) is negligible compared to (A10). Reaction (A14) is slow relative to (A13) but is probably significant in systems with high concentrations of O_3. This reaction could be an important source of NO_3. Reaction (A15), the photolysis of O_3, is estimated to be only about 1/20 - 1/50 as fast as (A1) at similar concentrations. Reaction (A16) is negligible compared to (A9) and (A10).

Reactions (A17) to (A21) could occur in the presence of water vapor. Leighton[19] has suggested that appreciable fractions of the oxides of nitrogen could be hydrolyzed by (A17) and (A18) in a period of an hour or less, which is sufficiently rapid to warrant consideration in atmospheric systems. However, (A17) can be shown unimportant by equilibrium considerations. The direct hydrolysis of NO_2 by (A19) is quite slow. Reaction (A20) was postulated by Tuesday[33] to account for small amounts of N_2O in the photo-oxidation of trans-2-butene. The existence of the species HNO has not been confirmed, however, in photo-oxidation systems. Reaction (A21) is endothermic and thus quite slow compared to (A9) and (A10). Reactions (A23), (A24), and (A25) are unimportant.

The reactions can be separated according to their probable importance in photochemical smog:

a. Primary Importance: (A1,A2,A3).

b. Secondary Importance: (A4,A5,A7,A9,A12,A14,A15,A18).

c. Negligible Importance: (A6,A8,A10,A11,A13,A16,A17,A19,A20,A21, A22,A23,A24,A25).

The reaction of O atoms with SO_2 may play an important role in the production of SO_3 and subsequently H_2SO_4 in smog. H_2SO_4 will form aerosols with water. The reactions are

$$O + SO_2 \rightleftarrows SO_3^* \tag{A26}$$

$$SO_3^* + M \rightarrow SO_3 + M \tag{A27}$$

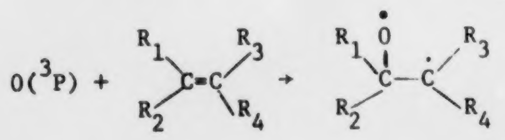
$$SO_3 + H_2O \rightarrow H_2SO_4 \tag{A28}$$

Reaction (A26) was studied by Jaffe and Klein[34] and by Kaufman.[35] It yielded a rate constant equal to 1.4 x 10^{10} $liter^2 mole^{-2} sec^{-1}$ for the over-all reaction

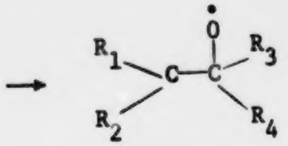
$$SO_2 + O + M \rightarrow SO_3 + M \tag{A29}$$

2. Reactions of Atomic Oxygen and Hydrocarbons

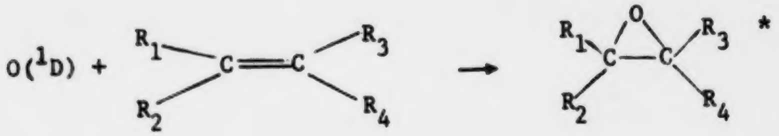
Compounds containing carbon-hydrogen bonds are particularly susceptible to attack by free oxygen atoms. Among the most reactive hydrocarbons are the olefins and other compounds containing olefinic double bonds. The elementary step is usually conceived as the addition of the oxygenation to the double bond to form an activated complex which may decompose in various ways. The general olefin-atomic oxygen reactions can be written as[21]



(B1)



(B2)



(B3)

The asterisk indicates that the complex possesses excess energy and will rapidly participate in further reactions or decomposition.

The reactions of oxygen atoms with paraffins are slower than with olefins. The most likely elementary step seems to be

$$RH + O \rightarrow R\cdot + \dot{O}H \qquad (B4)$$

with a rate constant of 10^5 to 10^7 l $mole^{-1}$ sec^{-1}.

Rate constants for the reactions of atomic oxygen and hydrocarbons have been compiled by Altshuller and Bufalini[21] and Cvetanovic.[36,37,38] Rate constants (l $mole^{-1}$ sec^{-1}) are shown in Table 4-11.

The probable reaction of aldehydes and atomic oxygen is

$$RCHO + O \rightarrow R\dot{C}O + \dot{O}H \qquad (B5)$$

with a rate constant the order of 10^8 l $mole^{-1}$ sec^{-1}.

Products from the decomposition of the activated complexes in (B1) to (B3) differ for the various olefins, but comprise principally the corresponding olefin oxides and aldehydes derived from them by slight rearrangement The following product distribution has been observed from the reaction of

Table 4-11. RATE CONSTANTS OF ATOMIC OXYGEN-HYDROCARBON REACTIONS.

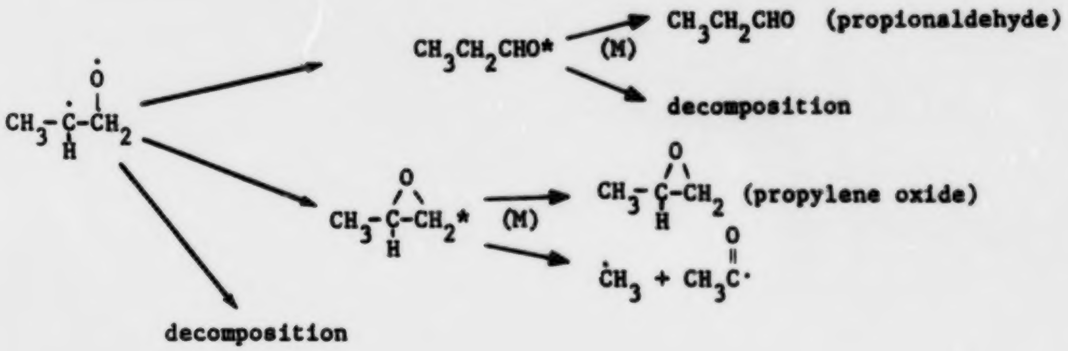
Hydrocarbon	Rate Constant (ℓ, mole, sec)	Reference
Ethylene	3.1×10^{8}	39,40
Propylene	1.7×10^{9}	*
1- Butene	1.7×10^{9}	*
Isobutene	7.5×10^{9}	*
Cis-2-butene	7.1×10^{9}	*
Trans-2-butene	8.5×10^{9}	*
n-1-pentene	3.1×10^{9}	*
cis-2-pentene	6.8×10^{9}	*
1-Hexene	1.95×10^{9}	*
Cyclopentene	1.46×10^{10}	*
Cyclohexene	1.32×10^{10}	36,37,38
2-Methyl-2butene	3.88×10^{10}	36,37,38
2,3-Dimethyl-2-butene	5.12×10^{10}	36,37,38
1,3-Butadiene	1.19×10^{10}	36,37,38
Benzene	1.98×10^{7}	36,37,38
Toluene	6.93×10^{7}	36,37,38
1,3,5 Trimethylbenzene	3.3×10^{8}	21
Styrene	5.0×10^{9}	21
3-Methylheptane	6.5×10^{7}	28

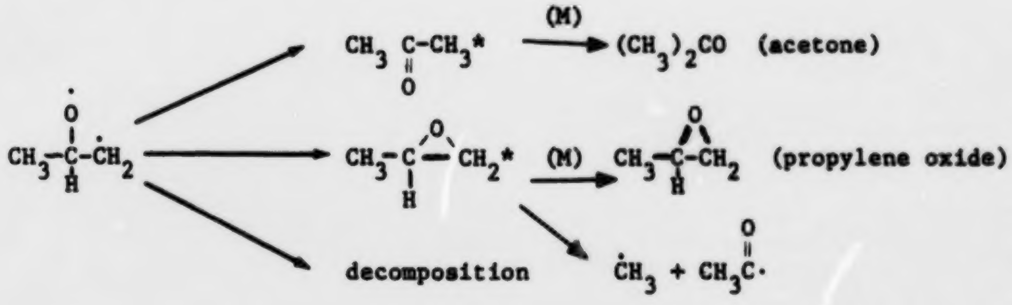
* Calculated from the relative rates of O + X vs. O + C_4H_8-iso, X=NO_2=0.44 from reference,[21] where k(O + NO_2) = 3.3 X 10^9/liter/mole^{-1}sec^{-1}.

from the reaction of ethylene and atomic oxygen:[19]

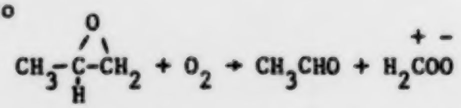
$$C_2H_4 + O \longrightarrow \left\{ \begin{array}{l} .03 \text{ polymer} \\ .03\ C_2H_4O \\ .05\ H_2 + CH_2 + CO \\ .04\ H_2 + CH_2CO \\ .10\ H + C_2H_3O \\ .75\ CH_3\cdot + H\dot{C}O \end{array} \right.$$

The activated complexes in (B1) and (B2) formed in the propylene-atomic oxygen reaction can participate in the following further reaction steps:[19]



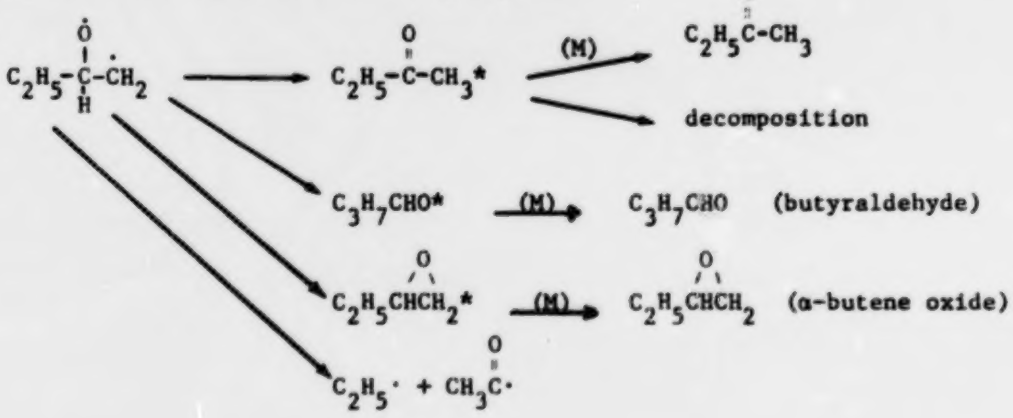


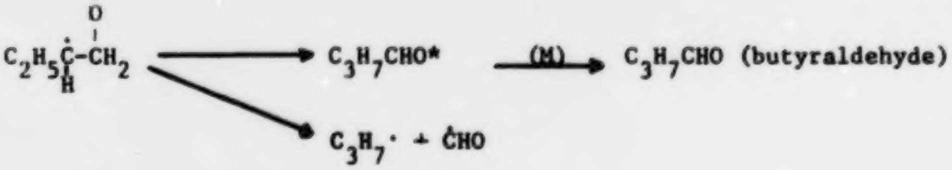
When molecular oxygen is present the propylene oxide will react with O_2, most likely according to



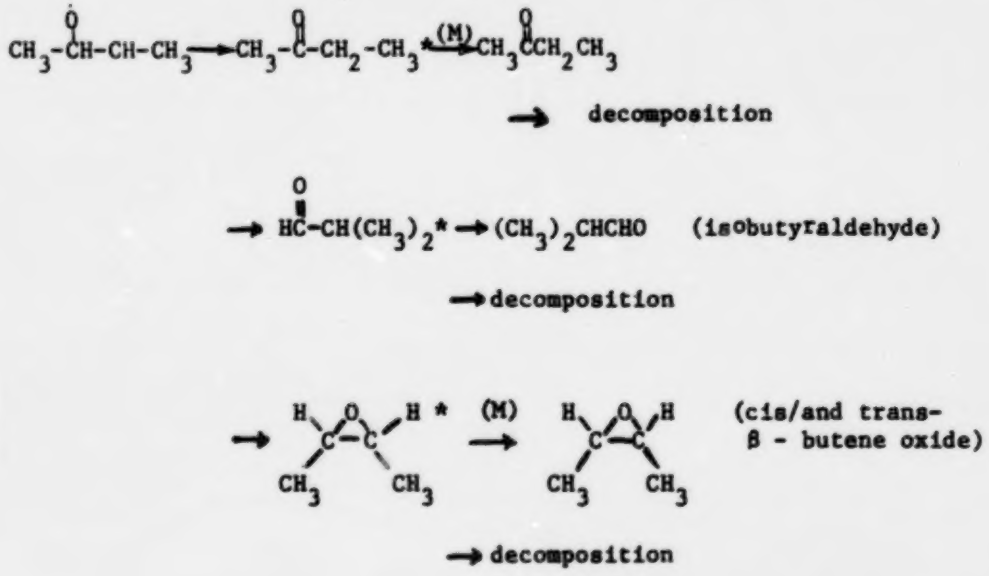
$$CH_3\text{-}\overset{O}{\widehat{CH\text{-}CH_2}} + O_2 \rightarrow CH_3CHO + H_2\overset{+}{C}O\overset{-}{O}$$

The reaction of 1-butene with atomic oxygen has been found to yield 57 percent α-butene oxide and 43 percent butyraldehyde.[36,37,38] The mechanism accounting for these products is similar to that for propylene:





Cis-2-butene and atomic oxygen yield 25 each cis-and trans-β-butene oxide, 22 percent isobutyraldehyde and 28 percent methyl ethyl ketone (2-butanone).[36,37,38] The probable mechanism for this reaction is again similar to those above and is:



$$CH_3-\overset{O}{C}H-CH-CH_3 \rightarrow CH_3-\overset{O}{\overset{\|}{C}}-CH_2-CH_3{}^{*} \xrightarrow{(M)} CH_3\overset{O}{\overset{\|}{C}}CH_2CH_3$$

$$\rightarrow \text{decomposition}$$

$$\rightarrow H\overset{O}{\overset{\|}{C}}-CH(CH_3)_2{}^{*} \rightarrow (CH_3)_2CHCHO \quad \text{(isobutyraldehyde)}$$

$$\rightarrow \text{decomposition}$$

The reactions for trans-2-butene are similar to those for cis-2-butene. Isobutene-atomic oxygen products include methyl ethyl betone, isobutene oxide and isobutyraldehyde.

Reactions of hydrocarbons and atomic oxygen can now be summarized. Only a minor fraction of the ethylene consumed when reacting with atomic oxygen yielded products with two carbon atoms. Fragmentation into methyl and formyl radicals is apparently the principal process. In the propylene-atomic oxygen reaction the main products are propylene oxide, propionaldehyde, acetone and small amounts of carbon monoxide. The main fragmentation process is probably to methyl and acyl radicals. The butenes yield butene oxides, butyraldehyde and methyl ethyl ketone. The main fragmentation process is expected to yield either propionyl and formyl radicals or ethyl and acyl radicals. In the presence of O_2 the products are typical of those in O_3 attack.

Recently, Klein and Sheer[30] have proposed a new transition state for the 2-methyl-2-pentene reaction with $O(^3P)$. They suggest a concerted rearrangement of the transition state rather than the formation of an actual biradical to obtain the products of the reaction.

3. Reactions of Ozone and Hydrocarbons

O_3 is a strong oxidizing agent and will react with hydrocarbons and other organics present in urban air. Olefins are readily attacked by O_3 in the vapor phase, the initial step of which is usually assumed to be addition of O_3 to the olefin molecule to form an energetic complex. The energetic complex can decompose or switch to its isomer through loss of some of the excess energy.

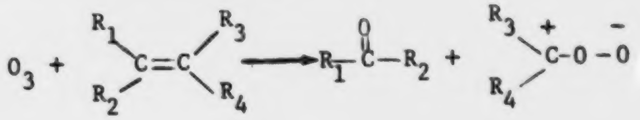
Rate constants for O_3-hydrocarbon reactions have been tabulated by Altshuller and Bufalini[21] and are shown in Table 4-12 Each column represents the results of particular investigators.

The rate constants for the 1-olefins with the exception of ethylene fall closely together, while those for the 2-olefins may be considerably higher.[20]

Table 4-12. RATE CONSTANTS FOR OZONE-HYDROCARBON REACTIONS (ℓ mole^{-1}sec^{-1})x10^3.

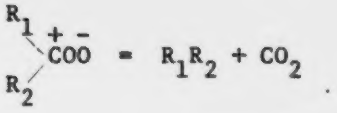
Hydrocarbon	References				
	42	43	44	45	21
Ethylene	1.8	1.8	0.8		1.6
Propylene	5.1	3.8	4.9		
1-Butene	3.9				3.2
n-1-Pentene	3.9	3.2	4.5		
n-1-Hexene	4.6	6.1	6.1	5.5	6.8
1-Octene		4.9			
1-Decene		6.6			
3-Methyl-1-butene	3.0				
Isobutene	3.6		3.7		14
2-Methyl-1-butene	4.0				
Cis-2-butene	13		29		200
Trans-2-butene	17				260
Trans-2-pentene	10		98		
Trans-2-pentene	13				
3-Heptene (cis-trans)			53		
Cyclohexene	14	35			
2-Methyl-2-butene	12				450
2,3-Dimethyl-2-butene	14				
1,3-Butadiene	4.2		4.9		
Acetylene		0.04			
Xylene			<0.01		
Mesitylene					<0.1
Styrene					18
Acrolein			0.45		
Crotonaldehyde			0.45		
Ketene			<0.04		

The products of the O_3-olefin reactions vary depending on the particular olefin. Prominent products include aldehydes, ketones and carboxylic acids. The most widely accepted reaction mechanism hypothesis is that the energetic intermediate formed from initial attack of O_3 on the olefin decomposes to produce a carbonyl compound and an unstable intermediate compound, sometimes called a zwitter ion. Thus, the initial reaction is

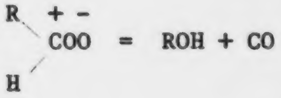


(C1)

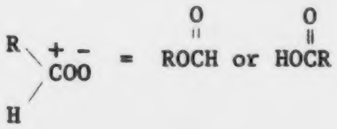
The zwitter ion is unstable and decomposes in various ways, among which may be:



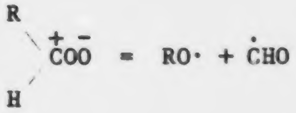
(C2)



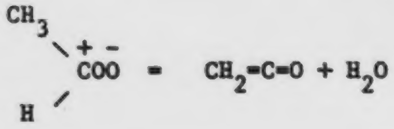
(C3)



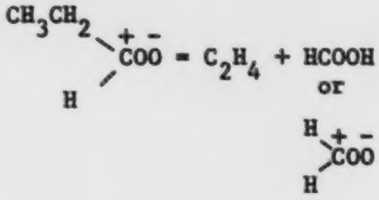
(C4)



(C5)



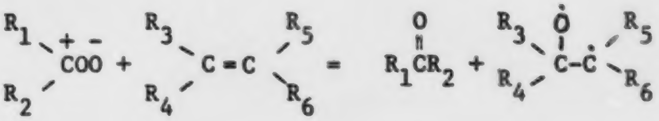
(C6)



(C7)

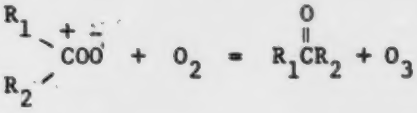
In addition to decomposition, the zwitter ion can participate in reactions with other species. Possibilities include:

Olefins

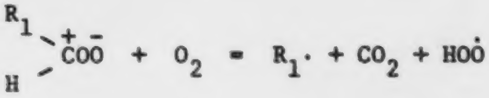


(C8)

Oxygen

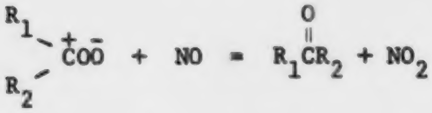


(C9)



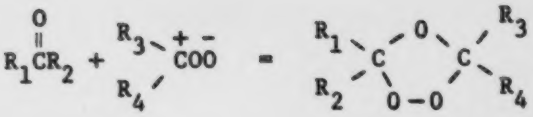
(C10)

NO



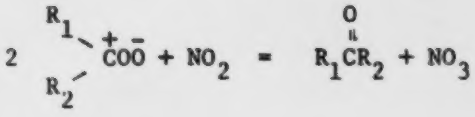
(C11)

Ketones



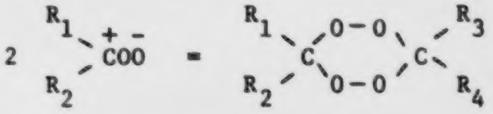
(C12)

NO_2



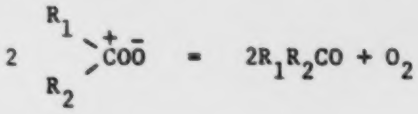
(C13)

In addition, two zwitter ions could react



(C14)

forming an alkylidene peroxide which, however, has not been observed. Another possible reaction between two zwitter ions is



(C15)

Mechanisms alternate to that of the zwitter ion have been proposed. A direct dissociation of the original activated complex to two free radicals has been suggested by Wayne.[20] It is unlikely, however that a large proportion of O_3-olefin collisions would yield free radicals directly.

4. Reactions Between Free Radicals and Molecular Oxygen or Ozone.

There is substantial evidence for the existence of chain reactions in the photochemical smog system. These chain reactions proceed with the aid of free radicals, the unpaired elections of which are preserved through the various steps of the chain even though the species with the unpaired electron may change from step to step.

Haagen-Smit, et al.[46] concluded that O_3 was formed in a chain reaction during the photo-oxidation of 3-methylheptane. They suggested that alkyl and peroxyalkyl radicals might be the chain-propagating species. Cadle[47] suggested that peroxyalkyl radical could be responsible for the conversion of NO to NO_2 in photo-oxidation systems. Schuck, et al.[48] compared the observed rates of consumption of olefins in photo-oxidation systems with the expected rates based on literature values for the reactions with O_3 and O. They found the observed rates much faster than the expected rates. They attributed the "excess rate" to reactions of the olefins with free radicals in the system. Tuesday[33] concluded that a free radical chain reaction initiated by reaction of oxygen atoms and olefin was important in the photo-oxidation of trans-2-butene and NO.

Wayne[20] has provided a clear explanation of the importance of chain reactions in photochemical smog. Since oxygen atoms are known to react very readily with olefins, it is feasible that the chain reactions be initiated by this reaction. However, only a fraction of the oxygen atoms generated can be assumed to react with olefins because of competition with the O_2 reaction. Also, the olefin-oxygen atom reaction yields a variety of products, not all of which are capable of propagating chains. For example, if only half of the oxygen atoms generated react with olefins and only one olefin molecule in five yields free radicals when it reacts with an oxygen atom, then a chain length of 60 would be necessary to account for an observed quantum yield of 6. Thus, only small amounts of NO_2 are required to initiate the process. As the small amount of NO_2 dissociates into NO and oxygen atoms, chains are initiated and NO_2 is produced from NO in a self-accelerating process. This is precisely the situation in early morning urban air, in which small quantities of NO_2 are capable of initiating the daily smog cycle.

Reactions responsible for the generation of free radicals have been outlined above, mainly from the hydrocarbon-oxygen atom and hydrocarbon-ozone reactions. One of the most probable steps is the fragmentation of the activated complexes in (B1), (B2) and (B3) to yield two free radicals, e.g., the production of methyl and formyl radicals from the ethylene-atomic oxygen reaction. Another example is the production of free radicals from atomic oxygen in (B4). Another possible source of free radicals is the decomposition of the activated complex from the olefin-ozone reaction as in (C5). In addition, reactions of the zwitter ion might yield free radicals (C8), (C10), as well as the photolysis of various organic compounds as shown in Table 4-4.

In this and succeeding subparagraphs, possible reactions of free radical species in polluted urban air are outlined. In each case a summary lists the most important reactions of each type. In this subparagraph the reactions of free radicals with molecular oxygen are outlined. For the most part, these are chain-propagating reactions which conserve the number of free radicals in the system. Reactions are listed by radical type.

a. Alkyl Radicals $R\cdot$

$$R\cdot + O_2\ (+M) = RO\dot{O}\ (+M) \tag{D1}$$

e.g., $$CH_3\cdot + O_2\ (+M) = CH_3O\dot{O}\ (+M)$$

b. Acyl Radicals $R\dot{C}O$

$$R\dot{C}O + O_2 = R\overset{\overset{\displaystyle O}{\|}}{C}O\dot{O}\ \text{(peroxyacyl)} \tag{D2}$$

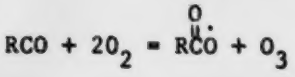
$$R\dot{C}O + O_2 = R\dot{O} + CO_2 \tag{D3}$$

e.g., $$H\dot{C}O + O_2 = \dot{O}H + CO_2$$

$$CH_3\dot{C}O + O_2 = CH_3\dot{O} + CO_2$$

$$R\dot{C}O + O_2 = RO\dot{O} + CO \tag{D4}$$

e.g., $H\dot{C}O + O_2 = HO\dot{O} + CO$

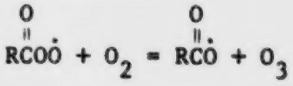


$$RCO + 2O_2 = R\overset{\overset{O}{\|}}{C}\dot{O} + O_3 \qquad (D5)$$

c. Peroxyalkyl Radicals $RO\dot{O}$

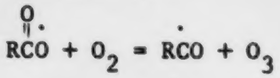
$$RO\dot{O} + O_2 = R\dot{O} + O_3 \qquad (D6)$$

d. Peroxyacyl Radicals $R\overset{\overset{O}{\|}}{C}O\dot{O}$

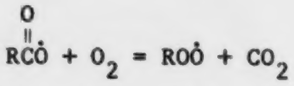


$$R\overset{\overset{O}{\|}}{C}O\dot{O} + O_2 = R\overset{\overset{O}{\|}}{C}\dot{O} + O_3 \qquad (D7)$$

e. Acylate Radicals $R\overset{\overset{O}{\|}}{C}\dot{O}$



$$R\overset{\overset{O}{\|}}{C}\dot{O} + O_2 = R\dot{C}O + O_3 \qquad (D8)$$



$$R\overset{\overset{O}{\|}}{C}\dot{O} + O_2 = RO\dot{O} + CO_2 \qquad (D9)$$

f. Alkoxyl Radicals $RO\cdot$

$$RO\cdot + O_2 = R'CHO + HO\dot{O} \qquad (D10)$$

$$RO\cdot + O_2 = R\cdot + O_3 \qquad (D11)$$

g. Hydroxyl Radical $H\dot{O}$

Does not react with O_2 at ordinary temperatures.

h. Hydroperoxyl Radicals $HO\dot{O}$

$$HOO\cdot + O_2 = O_3 + HO\cdot \qquad (D12)$$

i. Summary of Free Radical Reactions with O_2

Reaction (D1) is well substantiated as the most probable fate of alkyl radicals in an oxygen-containing environment. The rate constant is about 10^8 liter $mole^{-1}sec^{-1}$. Of the various reactions of acyl radicals with O_2, (D2) is probably most likely at ordinary temperatures. This reaction, the direct combination of acyl radicals and O_2 to form peroxyacyl radicals, is supported by the occurrence of PAN-type compounds in organic photo-oxidation systems. Taylor and Blacet [49] suggested (D3) and (D4) as possible reactions to compete with (D2). Reaction (D5) was suggested by Schuck and Doyle[50] to account for O_3 production.

Reaction (D6) has been often proposed to account for the production of O_3 in organic photo-oxidations.[20] In the oxidation of methyl radicals at room temperature, (D6) has been suggested as the principal route for destruction of peroxymethyl radicals. Since it is certainly endothermic by at least 20 Kcal, the collision yield can hardly be greater than 10^{-10}, unless the alkoxy radicals are available in a higher electronic state or a highly excited vibrational state. Such radicals with sufficient energy may be produced by reaction (D1), but they are probably highly susceptible to collisional deactivation. Reaction (D7) and (D8) analogous to (D5) have been proposed to account for the production of O_3 in urban air. Their relative importance is difficult to assess but, like (D6), they must be quite endothermic. Little evidence exists to support (D9), proposed by Stephens;[51] in contrast to (D8) it should be highly exothermic (ca. 50 Kcal) and thus might have a high collision yield.

Reaction (D10) has been suggested by Hanst and Calvert[52] to explain the production of formaldehyde in the photolysis of dimethyl peroxide in the presence of O_2. Taylor and Blacet[49] proposed (D10) as a competing reaction to (D11) in the photo-oxidation of biacetyl. Schuck, et al.[48] also suggested (D10) could be responsible for acetaldehyde production. Reaction (D11), since it involves the rupture of a carbon-oxygen bond to form an oxygen-oxygen bond, is even more endothermic than (D6) and is quite unlikely to be of any significance in urban atmospheres.

Some actual examples and rate constants are given in Table 4-13. The direct reaction of O_3 with radicals has been suggested by Calvert and Hanst[56] in the reaction

$$\dot{C}H_3 + O_3 = CH_3\dot{O} + O_2 \qquad \text{(D13)}$$

The rate constant for (D13) is estimated to be 5×10^9 to 10^{11} liter $\text{mole}^{-1}\text{sec}^{-1}$. The rates of heavier alkyl radicals with ozone are not known, but are probably of the same order of magnitude as that of methyl radicals. A similar reaction would be expected with hydrogen atoms,

$$H\cdot + O_3 = \dot{O}H + O_2 \qquad \text{(D14)}$$

but no rate data are available.

5. Reactions Between Free Radicals and NO

Nitric oxide may add to free radicals quite readily, since it itself

Table 4-13. SOME REACTIONS OF O_2 WITH FREE RADICALS.

Reaction	Rate Constant at 300°K	Preexponential Factor	Activation Energy	Collision* Yield	Reference
$CH_3 + O_2 \xrightarrow{+M} CH_3O_2$	$3x10^{10}$				53
$CH_3 + O_2 \longrightarrow CH_2O + HO$	$\sim 6x10^7$				54
$C_2H_5O + O_2 \longrightarrow CH_3CHO + HO_2$		10^8	5500		55
$C_2H_5 + O_2 \longrightarrow C_2H_4 + HO_2$	$10^{8.8}$				53
$RO_2 + O_2 \longrightarrow RO + O_3$		$10^{8.5}$	3500		55
$H + O_2 \xrightarrow{+M} HO_2$				$1x10^{-4}$	1

---

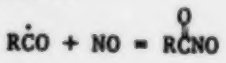
*Collision Yield = $\frac{k}{Z} = pe^{-E/RT}$

is an odd electron molecule. The requirement is that the excited adduct be stabilized by collisions, since the excited molecule formed would dissociate due to the exothermicity of the reaction.

a. Alkyl Radicals

$R\cdot + NO = RNO$ (E1)

b. Acyl Radicals



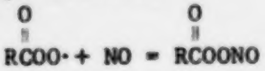
$R\dot{C}O + NO = R\overset{\overset{O}{\|}}{C}NO$ (E2)

c. Peroxyalkyl Radicals

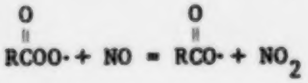
$RO\dot{O} + NO = ROONO$ (peroxyalkyl nitrite) (E3)

$ROO\cdot + NO = RO\cdot + NO_2$ (E4)

d. Peroxyacyl Radicals

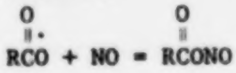


$R\overset{\overset{O}{\|}}{C}OO\cdot + NO = R\overset{\overset{O}{\|}}{C}OONO$ (peroxyacyl nitrite) (E5)

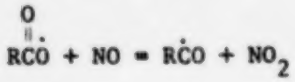


$R\overset{\overset{O}{\|}}{C}OO\cdot + NO = R\overset{\overset{O}{\|}}{C}O\cdot + NO_2$ (E6)

e. Acylate Radicals



$R\overset{\overset{O}{\|}}{C}\dot{O} + NO = R\overset{\overset{O}{\|}}{C}ONO$ (E7)



$R\overset{\overset{O}{\|}}{C}\dot{O} + NO = R\dot{C}O + NO_2$ (E8)

f. **Alkoxyl Radicals**

$$RO\cdot + NO = RONO \qquad (E9)$$

$$RO\cdot + NO = R'CHO + HNO \qquad (E10)$$

g. **Hydroxyl Radicals**

$$HO\cdot + NO = HONO \qquad (E11)$$

h. **Hydroperoxyl Radicals**

$$HO\dot{O} + NO = \dot{O}H + NO_2 \qquad (E12)$$

i. **Summary of Free Radical Reactions with Nitric Oxide**

(E1) is insignificant when compared to the combination of alkyl radicals and O_2. Also, (E2) is probably negligible when compared to the corresponding reaction with O_2, (D2). The peroxyalkyl nitrite product in (E3) has not been observed with certainty. It may be a short-lived product or a transition state for (E4). Such molecules probably undergo rapid photolysis to the original reactants or to the products of (E4), and are thus not important as chain-terminating species. Reaction (E4) has been proposed to explain the rapid conversion of NO to NO_2 in organic photo-oxidation systems.[19] Reaction (E4) is strongly exothermic and would be a possible important reaction.

The peroxyacyl nitrite product in (E5) has not been observed. Reaction (E6), analogous to (E4), is strongly exothermic and believed to occur. A plausible argument for the delayed appearance of PAN in such systems is that (E6) successfully competes with the PAN-forming reaction (F5) until all the NO is consumed. The product in (E7) has not been observed. Reaction (E8), similar to (E6), would be highly exothermic and a possible route for conversion of NO to NO_2.

Reaction (E9) may well be occurring with a high collision yield. However, the alkyl nitrite product is seldom observed because of its high efficiency of photodissociation. Reaction (E10) has been postulated to explain the decrease in oxidation rate in the presence of excess NO. Little evidence of the importance of (E11), analogous to (E9), is available. Reaction (E12), like (E4), is strongly exothermic and possibly important in urban atmospheres.

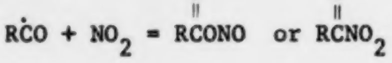
6. Reactions Between Free Radicals and NO_2

a. Alkyl Radicals

$$R\cdot + NO_2 = RNO_2 \tag{F1}$$

$$R\cdot + NO_2 = \dot{R}O + NO \tag{F2}$$

b. Acyl Radicals

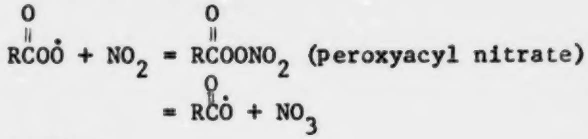


$$R\dot{C}O + NO_2 = R\overset{\overset{O}{\|}}{C}ONO \text{ or } R\overset{\overset{O}{\|}}{C}NO_2 \qquad (F3)$$

c. Peroxyalkyl Radicals

$$RO\dot{O} + NO_2 = R\dot{O} + NO_3 \qquad (F4)$$

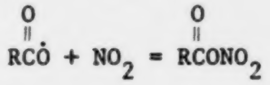
d. Peroxyacyl Radicals



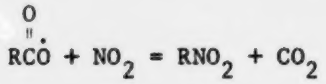
$$R\overset{\overset{O}{\|}}{C}O\dot{O} + NO_2 = R\overset{\overset{O}{\|}}{C}OONO_2 \text{ (peroxyacyl nitrate)} \qquad (F5)$$

$$= R\overset{\overset{O}{\|}}{C}\dot{O} + NO_3 \qquad (F6)$$

e. Acylate Radicals



$$R\overset{\overset{O}{\|}}{C}\dot{O} + NO_2 = R\overset{\overset{O}{\|}}{C}ONO_2 \qquad (F7)$$



$$R\overset{\overset{O}{\|}}{C}\dot{O} + NO_2 = RNO_2 + CO_2 \qquad (F8)$$

f. Alkoxyl Radicals

$$R\dot{O} + NO_2 = RONO_2 \text{ (alkyl nitrate)} \qquad (F9)$$

$$R\dot{O} + NO_2 = R\dot{O}_2 + NO \qquad (F10)$$

g. Hydroxyl Radicals

$$\dot{O}H + NO_2\ (+M) = HNO_3(+M) \qquad (F11)$$

h. Hydroperoxyl Radicals

$$H\dot{O}O + NO_2 = NO_3 + \dot{O}H \tag{F12}$$

i. Summary of Free Radical Reactions with NO_2

Reactions of (F1) and (F2) probably cannot compete with (D1). Nevertheless, the nitroalkane product of (F1) is relatively stable to photolysis and, at low O_2 concentrations, could be a chain terminating step. Reaction (F3) is probably negligible compared to (D2).

Reaction (F4) is considerably less exothermic than the corresponding NO reactions, (E4) and (E6). It is probable that this reaction will be slower than (E4) and (E6) by a factor of 10^3 at equivalent concentrations.[19] Similarly, (F6) is not favored energetically by comparison to (E4) and (E6). Reaction (F5) is probably quite important, yielding peroxyacyl nitrates when the concentration ratio $(NO_2)/(NO)$ becomes large.

Reaction (F7) and (F8) are probably both unimportant compared to the decomposition of acylate radicals. Reaction (F9) may be an important chain-terminating step. It has been generally postulated to account for the occurrence of alkyl nitrates among the products of photo-oxidation systems. An alternate reaction to (F9) is (F10), with a collision yield about twice as great.

Reaction (F11) has been suggested as a chain-terminating step for hydroxyl radicals, although nitric acid has not been commonly recognized as a product in photo-oxidations. Reaction (F12) is analogous to (F4), but is energetically less favored.

Table 4-14 presents rate constants, activation energy and collision yield data for some reactions of free radicals with NO and NO_2.

7. Reactions Between Free Radicals and Hydrocarbons

a. Alkyl Radicals

$R\cdot + XH = RH + X.$ (Hydrogen-Abstraction) (G1)

$R_1\cdot + R_2CHO = R_1H + R_2\dot{C}O$ (G2)

$R\cdot + O\ell = RO\ell\cdot$ (G3)

b. Acyl Radicals

$R\dot{C}O + O\ell = (RCO)O\ell$ (G4)

c. Peroxyalkyl Radicals

$R_1O\dot{O} + R_2H = R_1OOH + \dot{R}_2$ (G5)

$R_1O\dot{O} + R_2CHO = R_1OOH + R_2\dot{C}O$ (G6)

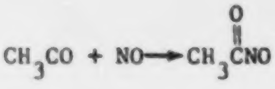
$ROO\cdot + O\ell = (ROO)O\ell\cdot$ (G7)

$RO\dot{O} + XH = ROOH + X\cdot$ (G8)

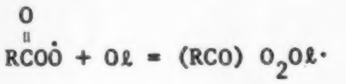
---

* Oℓ here represents an olefin molecule. Addition of the radical takes place on one of the double-bonded carbon atoms, with the other acquiring the odd electron, e.g., $CH_3\cdot + H_2C = CH_2 = CH_3CH_2\dot{C}H_2$.

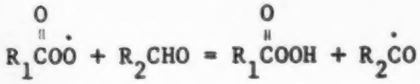
Table 4-14. SOME REACTIONS OF NO AND NO_2 WITH FREE RADICALS.

Reaction	Rate Constant at 300°K	Activation Energy	Collision Yield	Reference
$CH_3 + NO \rightarrow CH_3NO$	6.3×10^{8}			57
 $CH_3CO + NO \rightarrow CH_3\overset{\overset{O}{\parallel}}{C}NO$			10^{-4}	1
$(CH_3)_3CO + NO \rightarrow (CH_3)_3CONO$		~13.2 ± 2.4		58
$CH_3 + NO_2 \rightarrow CH_3NO_2$	1.7×10^{9}			56
$CH_3 + NO_2 \rightarrow CH_3O + NO$	3.3×10^{9}			56

d. Peroxacyl Radicals

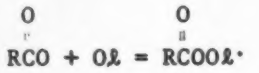


$$R\overset{\overset{O}{\|}}{C}O\dot{O} + O\ell = (RCO)\ O_2O\ell\cdot \qquad \text{(G9)}$$

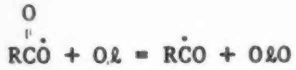


$$R_1\overset{\overset{O}{\|}}{C}O\dot{O} + R_2CHO = R_1\overset{\overset{O}{\|}}{C}OOH + R_2\dot{C}O \qquad \text{(G10)}$$

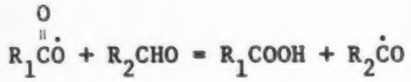
e. Acylate Radicals



$$R\overset{\overset{O}{\|}}{C}O + O\ell = R\overset{\overset{O}{\|}}{C}OO\ell\cdot \qquad \text{(G11)}$$



$$R\overset{\overset{O}{\|}}{C}\dot{O} + O\ell = R\dot{C}O + O\ell O \qquad \text{(G12)}$$



$$R_1\overset{\overset{O}{\|}}{C}\dot{O} + R_2CHO = R_1COOH + R_2\dot{C}O \qquad \text{(G13)}$$

f. Alkoxyl Radicals

$$RO\cdot + O\ell = (RO)O\ell\cdot \qquad \text{(G14)}$$

$$R\dot{O} + XH = ROH + X\cdot \qquad \text{(G15)}$$

$$R_1\dot{O} + R_2CHO = R_1OH + R_2\dot{C}O \qquad \text{(G16)}$$

g. Hydroxyl Radicals

$$HO\cdot + O\ell = (HO)O\ell\cdot \qquad \text{(G17)}$$

$$\dot{O}H + XH = H_2O + X\cdot \qquad (G18)$$

$$\dot{O}H + RCHO = H_2O + R\dot{C}O \qquad (G19)$$

h. Hydroperoxyl Radicals

$$HO\dot{O} + Q\ell = (HOO)O\ell\cdot \qquad (G20)$$

$$HO\dot{O} + RCHO = RCO\cdot + H_2O_2 \qquad (G21)$$

i. Summary of Free Radical Reactions with Hydrocarbons

Of the three reactions (G1), (G2), and (G3), (G3) is the most favored, although none of the three can compete with (D1) in the urban atmosphere. Reaction (G4) is probably slow when compared to (D2), but might account in part for the existence of olefin polymers and co-polymers in liquid phase products in the form of aerosol particles.

Reactions (G5) and (G6) are probably unimportant at room temperature. Reaction (G7) has been proposed as the gas phase analog of the free radical reaction which initiates polymerization in liquid-phase olefin reaction, and could be part of a chain which yields aldehydes and ketones as products.[19]

Reactions (G9), (G11), (G14), and (G17) are similar to (G4) and can account for the presence of higher molecular weight oxidation products. However, (G9) and (G10) probably cannot compete with (E6) and (F5).

Reactions (G15) and (G16) probably do not compete successfully with (G14). Of the various hydrogen abstraction reactions, (G8) is the least favored and (G19) the most favored energetically. Reaction (G21) has been suggested as part of a mechanism in which the hydroperoxyl radical was a main chain-carrying species.

8. Reactions Between Free Radicals

a. Alkyl Radicals

$$R_1\dot{C}H_2 + R_2CH_2\dot{C}H_2 = R_1(CH_2)_3R_2 \qquad (H1)$$

$$R_1\dot{C}H_2 + R_2CH_2\dot{C}H_2 = R_1CH_3 + R_2CH{=}CH_2 \qquad (H2)$$

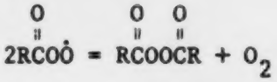
b. Acyl Radicals

See Reaction (H11).

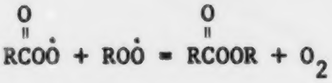
c. Peroxyalkyl Radicals

$$2RO\dot{O} = 2R\dot{O} + O_2 \qquad (H3)$$

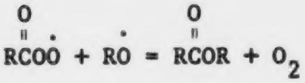
d. **Peroxyacyl Radicals**



$$2R\overset{O}{\overset{\|}{C}}O\dot{O} = R\overset{O}{\overset{\|}{C}}OO\overset{O}{\overset{\|}{C}}R + O_2 \tag{H4}$$

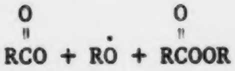


$$R\overset{O}{\overset{\|}{C}}O\dot{O} + RO\dot{O} = R\overset{O}{\overset{\|}{C}}OOR + O_2 \tag{H5}$$

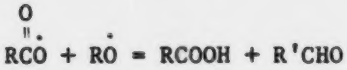


$$R\overset{O}{\overset{\|}{C}}O\dot{O} + R\dot{O} = R\overset{O}{\overset{\|}{C}}OR + O_2 \tag{H6}$$

e. **Acylate Radicals**



$$R\overset{O}{\overset{\|}{C}}O + R\dot{O} + R\overset{O}{\overset{\|}{C}}OOR \tag{H7}$$



$$R\overset{O}{\overset{\|}{\dot{C}}}O + R\dot{O} = RCOOH + R'CHO \tag{H8}$$

f. **Alkoxyl Radicals**

$$2R\dot{O} = ROOR \tag{H9}$$

$$2R\dot{O} = ROH + R'CHO \tag{H10}$$

$$R\dot{O} + R\dot{C}O = ROR + CO \tag{H11}$$

$$R\dot{O} + RO\dot{O} = ROR + O_2 \tag{H12}$$

g. **Hydroxyl Radicals**

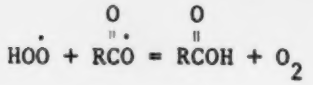
$$2\dot{O}H = H_2 + O_2 \tag{H13}$$

h. **Hydroperoxyl Radicals**

$$2HO\dot{O} = H_2O_2 + O_2 \tag{H14}$$

$$HO\dot{O} + RO\dot{O} = ROOH + O_2 \qquad (H15)$$

$$HO\dot{O} + RO\dot{O} = R\dot{O} + \dot{O}H + O_2 \qquad (H16$$



$$HO\dot{O} + R\overset{O}{\overset{\|}{C}}\dot{O} = R\overset{O}{\overset{\|}{C}}OH + O_2 \qquad (H17)$$

$$HO\dot{O} + R\dot{O} = ROH + O_2 \qquad (H18)$$

i. Summary of Reactions Between Free Radicals

Reactions (H1) and (H2) are negligible compared to the reaction with O_2, (D1). Reaction (H3) is possibly important but must compete with (D6), (E4), and (G7). Reactions (H4), (H5) and (H6) are, for the most part, negligible compared to the other reactions of peroxyacyl radicals. Reactions (H7) and (H8) are probably unimportant, as evidenced by the lack of esters in urban air. The disproportionation reaction (H10) is much faster than the combination reaction (H9). Reaction (H13) has been suggested as a chain termination step in mechanisms involving hydroxyl and hydroperoxyl radicals, but is probably unimportant in urban air. Of the reactions (H14) to (H18), the reactions most likely to be of importance are (H14) and (H18).

It should be noted that radical-radical reactions, although in general very fast, are restricted by the low concentrations of radicals, which lead to low collision frequencies.

Table 4-15 presents rate constants for some reactions between free radicals.

9. Radical Decomposition Reactions

a. Alkyl Radicals

No decomposition reaction.

b. Acyl Radicals

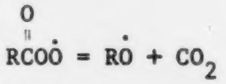
$$R\dot{C}O(+M) = R\cdot + CO(+M) \qquad (I1)$$

c. Peroxyalkyl Radicals

$$RCH_2O\dot{O} = RCHO + \dot{O}H \qquad (I2)$$

$$RCH_2O\dot{O} = R\dot{C}O + H_2O \qquad (I3)$$

d. Peroxyacyl Radicals

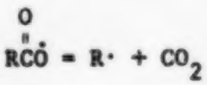


$$R\overset{O}{\overset{\|}{C}}O\dot{O} = R\dot{O} + CO_2 \qquad (I4)$$

Table 4-15. SOME FREE REACTIONS WITH FREE RADICALS.

Reaction	Rate Constant	Reference
$\dot{C}H_3 + \dot{C}H_3 \longrightarrow C_2H_6$	$10^{10.34}$ liter $mole^{-1} sec^{-1}$	59
$2\ CH_3\dot{O}_2 \longrightarrow 2\ CH_3\dot{O} + O_2$	$10^{10.2}$ or $10^{9.4}$	55
$CH_3\dot{O}_2 + H\dot{O}_2 \longrightarrow CH_3OOH + O_2$	$10^{9.5}$	55
$CH_3\dot{O}_2 + CH_3\dot{O} \longrightarrow CH_3OOH + CH_2O$	$10^{9.2}$	55
$CH_3\dot{O}_2 + \dot{O}H \longrightarrow CH_3OH + O_2$	$<10^{7}$	55
$CH_3\dot{O}_2 + \dot{R} \longrightarrow CH_3OOH$ + olefin	$10^{9.5}$	55
$CH_3\dot{O} + \dot{C}H_3 \longrightarrow CH_3OCH_3$	$10^{9.8}$	55
$CH_3\dot{O} + \dot{C}H_3 \longrightarrow CH_2O + CH_4$	$10^{10.0}$	55
$2CH_3\dot{O} \longrightarrow CH_3OH + CH_2O$	$10^{9.8}$	55
$2CH_3\dot{O} \longrightarrow (CH_3O)_2$	$10^{8.8}$	55

e. Acylate Radicals



$$R\overset{\overset{O}{\|}}{C}\dot{O} = R\cdot + CO_2 \qquad (I5)$$

f. Alkoxyl Radicals

$$R\dot{O} = R'CHO + R''\cdot \qquad (I6)$$

g. Hydroxyl Radicals

No decomposition reaction.

h. Hydroperoxyl Radicals

No decomposition reaction.

i. Summary of Radical Decomposition Reactions

The activation energy for the decomposition of acyl radicals by (I1) is quite high. It is probably not fast enough to exclude the competing reaction of acyl radicals with O_2, (D2). Reaction (I1) might be favored by the larger acyl radicals. The role of reactions (I2) and (I3) in urban air is uncertain, as is the role of reaction (I4).

There is a strong possibility that (I5) is the major process for acylate radicals in air, particularly if they are formed with excess energy. The rate of reaction (I6) may be competitive with the rates of the reactions of alkoxyl radicals with NO and NO_2, (E10) and (F9).

10. Summary of Important Reactions of Radicals

The most important reactions by radical type are:

1. Alkyl radicals react almost exclusively with O_2 in (D1).
2. Acyl radicals probably react exclusively with O_2 in (D2).
3. Peroxyalkyl radicals
    a) (D6) may be important if the radical has access emergency.
    b) Otherwise, (E4), (G7, G8, G9) and (F5) are likely to be important.
4. Peroxyacyl radicals probably participate in (D7), (F4), and (F5).
5. Acylate radicals probably undergo decomposition as in (I5).
6. Alkoxyl radicals
    a) (D10) can occur from photolysis of the alkyl nitrite from (E4).
    b) (E10) might help to explain the oxidation decrease with excess NO.
    c) (F9) is probably occurring in most systems to some extent.
    d) (G14) may help to explain excess rates.
    e) (I6) may be competitive with (E9), (E10), and (F9).
    f) Little is known about (H9) to (H12).
7. Hydroxyl radical reactions are not well elucidated as to relative importance.
8. Hydroperoxyl radicals probably participate in (F11), (G20), (H14), and (H18).

E. PHYSICAL AND CHEMICAL PROPERTIES OF THE PHOTOCHEMICAL REACTION PRODUCTS

The major products[60, 61] that result from the irradiation of NO, NO_2, and various olefins in air are ozone, peroxyacyl nitrates, aldehydes, ketones and carbon monoxide. The minor products include epoxides, nitric acid, alkyl nitrates and nitrites, peroxy compounds, methanol and ketene. In the presence of sulfur dioxide, sulfuric acid is also formed.

Some of the chemical and physical properties of these substances are listed here to help in their detection and identification or analysis. Some of these compounds can be recognized in the atmosphere by characteristic odors and chemical effects even though they are present in very low concentrations.

A short description of each compound follows, and some relevant properties are summarized in Table 4-16.

1. Ozone

Ozone is the most abundant oxidant in photochemical smog. It is thermodynamically unstable and highly reactive. It is a strong oxidizing agent, attacking rubber, textiles, plants and animal tissue. Ozone may be recognized by its pungent odor which resembles hay at low concentrations (pphm range) and the characteristic electrical arc welding odor at the ppm range.

2. Peroxyacyl Nitrates[61, 62, 63, 64]

The peroxyacyl nitrates are a series of thermodynamically unstable oxidants presumably formed by the combination of NO_2 with various peroxyacyl radicals. The pure compounds decompose slowly on standing at room temperature, or explosively, under some circumstances. Ultraviolet light also accelerates decomposition. They are very reactive and cause plant damage and eye irritation.

Table 4-16. SOME PROPERTIES OF PHOTOCHEMICAL REACTION PRODUCTS.

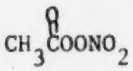
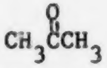
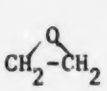
Substance	Chemical Formula	Molecular Weight g/mole	Physical State at 25°C	Melting Point Deg. C.	Boiling Point Deg. C.	Equilibrium Vap. Press. at 25°C	Remarks
Ozone	O_3	43	Odorless Gas	-192.1 (-251)	-112	>1 atm.	
Peroxyacetyl Nitrate	 $CH_3\overset{O}{C}OONO_2$	121	Colorless Liquid	--	Decomposes	~15mm Hg	One of an homologous series, PAN, PPN, PBN, etc.
Nitrogen Dioxide	NO_2	46	Brown-Red Gas	- 9.3	21	>1 atm.	Yellow liquid as N_2O_4 No true B.P. or M.P.
Formaldehyde	HCHO	30	Colorless Gas	- 92	- 21	>1 atm.	Polymerizes readily to paraformaldehyde
Acrolein	$CH_2=CHCHO$	56	Colorless Liquid	- 88	53	~300mm Hg	Well known lacrimator
Acetone	 $CH_3\overset{O}{C}CH_3$	58	Colorless Liquid	- 94.6	56.5	~300mm Hg	
Ethylene Oxide	 CH_2-CH_2	44	Colorless Liquid or gas	-111.3	10.7	>1 atm.	Example of simple epoxide
Methyl Nitrate	CH_3ONO_2	77	Colorless Liquid	--	65 exp	--	Explodes or decomposes before boiling
Methyl Nitrite	CH_3ONO	61	Colorless Gas	- 17.0	- 12	>1 atm	Example of simple nitrites

Table 4-16. SOME PROPERTIES OF PHOTOCHEMICAL REACTION PRODUCTS (Continued).

Substance	Chemical Formula	Molecular Weight gm/mole	Physical State at 25°C	Melting Point Deg. C.	Boiling Point Deg. C.	Equilibrium Vap. Press. at 25°C	Remarks
Hydrogen Peroxide	H_2O_2	34	Blue Liquid	-89	152.1	~8mm Hg	Example of simple peroxide
Methanol	CH_3OH	32	Colorless Liquid	- 97.8	64.65	~100mm Hg	
Ketene	$CH_2=C=O$	42	Colorless Gas	-151	-56	>1 atm	Example of Series of Ketenes
Nitric Acid	HNO_3	63	Colorless Liquid	- 42	86	~20mm Hg	
Sulfuric Acid	H_2SO_4	98	Colorless Liquid	10.5	330	~0	Boils with Decomposition

3. Oxides of Nitrogen, NO_x[69]

Seven known oxides of nitrogen are listed in Table 2-18. Of these NO_x compounds, only NO and NO_2 are abundant in the air and of major importance in photochemical smog. N_2O_5 may also play a minor role by its reaction with water to form nitric acid (HNO_3).

Nitric oxide is a colorless, odorless gas which is not a photochemical reaction product nor an oxidant, but is a precursor in formation of nitrogen dioxide.

Nitrogen dioxide is an oxidizing gas that is strongly toxic to plant and animal tissues. It can be recognized by its brownish color and its characteristic odor. Although NO_2 itself reacts slowly as an oxidant, its photodissociation produces oxygen atoms which, along with ozone, produce most of the photo-oxidation products found in smog.

4. Aldehydes and Ketones

Aldehydes and ketones are among the principal carbon-containing products resulting from the oxidation of hydrocarbons by oxygen atoms and ozone. They are dissociated by ultraviolet sunlight with the production of free radicals. Formaldehyde and acrolein, among the aldehydes, are known to cause eye irritation in smog. They can be oxidized slowly, mainly to organic acids; with or without oxidation, they show a strong tendency to polymerize and to be absorbed on particulate matter.

5. Carbon Monoxide

Carbon monoxide is a colorless, odorless gas that is extremely toxic at high concentrations. It is a product of incomplete combustion in internal combustion engines as well as a product of photochemical smog. It is rather inert chemically, oxidizing to CO_2 very slowly upon reaction with oxygen atoms or certain free radicals. It is generally considered a primary pollutant, since only relatively small concentrations can be photochemically generated.

6. Nitric Acid

Nitric acid vapor may be present in smog as a result of the reaction of N_2O_5 with water. Pure nitric acid is a colorless liquid at room temperature. It slowly decomposes to form NO_2, which in turn absorbs sunlight and hastens decomposition. The pure gaseous acid is a strong oxidizing agent, attacking metals and many organic substances. Ultraviolet photolysis of HNO_3 may be a source of OH radicals in the atmosphere.

7. Sulfuric Acid

Sulfuric acid, H_2SO_4, is an oily, exceedingly corrosive, nonvolatile liquid which results from the oxidation of sulfur dioxide in the presence of water vapor. It may play an important role in the formation of aerosols in photochemical smog. It is miscible in all proportions with water and is very highly hygroscopic. Droplets of sulfuric acid suspended in air, therefore, grow or shrink as the relative humidity of the air increases or decreases.

8. Aerosols[65]

Atmospheric particulates are mainly in the range of 0.05 to about 10μ in size. They are capable of acting as condensation centers. They consist of solid matter, droplets of solution, insoluble smokes and mineral dusts. The presence of NH_4^+ and $SO_4^=$, H_2SO_4, Cl^-, NO_3^- and other minor components in the solution phase have been reported, the composition varying with size and geographical location. Hygroscopic salts may be the origin of the ions in the particles.

The relation of aerosol loading to photochemical air pollution has been reviewed by Altshuller and Bufalini.[21] Mader, et al.[66] found high organic loadings in atmospheric aerosols collected in Los Angeles. Studying synthetic aerosols from irradiated mixtures containing gasoline vapor and nitrogen oxides in air, they found similar organic components. Infrared and chemical analysis of both types of aerosols showed the presence of carbonyl, hydroxyl, nitrate ester, peroxy, and carboxy groups. Renzetti and Doyle[67] showed that in irradiated mixtures of auto exhaust in air, large amounts of organic aerosols were produced. Schuck, et al.[70] showed that aerosols were produced more copiously in such experiments when the exhaust gases were derived from fuels of high olefinic content. It thus appears that at least some fraction of the aerosols found in ambient photochemical smog is generated by the photochemical reactions.

9. Epoxides

Cyclic ethers such as ethylene oxide may be formed to a small extent. Ethylene oxide is a colorless gas at 25°C. It is a fumigant and insecticide but not dangerously toxic to humans.

10. Alkyl Nitrates

Alkyl nitrates, such as ethyl nitrate, have pleasant fruity odors. They are unstable towards heat and will decompose explosively before boiling.

11. Alkyl Nitrites

Ethyl nitrite is a colorless gas at room temperature. Higher molecular weight nitrites, such as isoamyl nitrite, are physiologically active, producing in humans a fall in blood pressure and an acceleration of the heart rate.

12. Peroxy Compounds

Hydrogen peroxide is the simplest of the peroxy compounds and serves as an example of their behavior. It is a pale blue, syrupy liquid that is so unstable that it decomposes explosively at its normal boiling point. Dissociation by light of H_2O_2 and R_2O_2 compounds yields HO radicals and RO radicals, both of which are involved in the secondary processes in smog.

13. Alcohols

Methanol is a colorless liquid at room temperature with a faint odor, toxic by inhalation or ingestion. Higher alcohols, such as ethanol, are less volatile and less toxic; they are not very reactive compared with the other major products of photochemical smog.

14. Ketene

Ketene is a colorless gas with an unpleasant odor. It is a highly toxic and highly reactive compound. It reacts readily with such mild agents as ethanol, water, ammonia, and acetic acid. It has been suggested, but not detected, as a product in photochemical smog.

F. COMPUTER SIMULATION OF CHEMICAL KINETICS

1. Rationale for Kinetic Simulation

The classical task of chemical kinetics is the discovery of the mechanism of a complex reaction--that is, the formulation of a set of elementary reactions, postulated as occurring in a reaction system, such that the observed kinetic behavior of the components of the system can be shown to be a consequence of the simultaneous occurrence of all the individual reactions of the set.

The photochemical origin of ozone and other oxidants in polluted urban atmospheres was first recognized over twenty years ago. Since then, hundreds of experiments have been performed with synthetic smog, and dozens of elementary reaction steps and partial kinetic mechanisms have been discussed. As a result, substantial agreement has emerged with respect to most of the chemical principles involved, and many important aspects of the reaction mechanisms have been clarified.

Nevertheless, the task of theoretical interpretation of the photochemical smog phenomenon is incomplete, largely because of the chemical complexity of the systems that have to be studied. Most of the complex reactions whose kinetic behaviors have been successfully explained by traditional methods have been found to require mechanisms consisting of only a few elementary reactions, and involving only a few molecular species, including the reactants and observed products. Indeed, it is only for such relatively small sets of elementary reactions that the algebra involved could be analytically solved or conveniently manipulated.

For example, Shepp[71], who studied the photolysis of acetone, was able to demonstrate the applicability of a mechanism involving five elementary reactions and eight molecular species, including one reactant, four observed products and three postulated free radical intermediates. When the experimental conditions were restricted to temperatures above 100°C and relatively high light intensities, observed product concentrations were consistent with the algebraic expressions analytically derived from the mechanism. Experiments involving intermittent light, pulsed at various intervals, permitted him to estimate rate constants for the individual elementary reactions, even though the concentrations of the free radical species were not independently known. Although other reactions besides the five postulated are known to occur in such systems, the investigator was able to minimize their effect in the system by a judicious choice of experimental conditions.

By contrast, dealing with the photo-oxidation of even a single hydrocarbon with oxides of nitrogen in air requires postulating a mechanism of dozens of elementary reactions. Since each postulated reaction furnishes one additional differential equation to the collection, the mathematical analysis needed for their simultaneous solution becomes impractical.

In effect, this situation has been solved by the use of the high-speed numerical analysis capability of the modern digital computer, together with the accumulated body of experimental kinetic information and validated theory concerning elementary reactions of molecules, atoms and free radicals. Briefly, the system is to utilize the high-speed capability by postulating a large number of elementary reactions which may be thought important in the chemical system; to provide the computer with known or theoretical rate constants for each, together with initial concentrations for all main components; and to generate therefrom (by numerical integration) the expected kinetic behavior of all the reactants, products and intermediates known or suspected to be present in the system.

A particular advantage of such computerized analysis is that, in principle, it is unnecessary to make a priori judgments as to the relative importance of alternative reaction sequences in accounting for utilization or formation of the participating molecular species. Since the computer does not develop analytical solutions to the simultaneous differential equations, the inclusion of unnecessary elementary reactions does not interfere with the solution process. Consequently, if there is uncertainty regarding the importance of a proposed elementary reaction, it may be investigated by including the reaction in the set to be tested. If the rate of occurrence is negligible relative to that of other reactions in the set, this will become apparent on examination of the behavior of the specific rates as a function of simulated time, and the reaction in question can then be deleted from the set. Thus the numerical integration routine furnishes a sort of automatic correction procedure for the elimination of unnecessary steps from the postulated set.

Nevertheless, it is undesirable to expand the set of elementary reactions unnecessarily, since this would consume extra computing time.

2. The Basic Simulation Process

When the elementary reactions which can take place in a chemical system are known, together with their corresponding rate constants, it is a straightforward procedure to calculate rates of change of concentration of all reactant and product species, provided the concentrations are known for some specified instant of time. This is done for each species by calculating (using equation 4-29) the rate of consumption for each elementary reaction in which it is consumed and the rate of production for each elementary reaction in which it is produced. A negative sign is affixed for each of the consumption rate terms, and the net rate of concentration change is then the total of all the terms (with their appropriate signs).

A systematic procedure is to list and number the individual components of the reaction system as well as the individual elementary reactions, then use the stoichiometric coefficients of the reactions in the form of a matrix. An illustration of this procedure is shown in Table 4-17. A zero entry at the intersection of a row and a column indicates that the component corresponding to the column is not involved in the reaction corresponding to the row of entry. An entry with a positive sign indicates that the component is produced by the elementary reaction step, while an entry with a negative sign indicates that it is consumed. A numerical value of _1_ indicates that only one molecule of the component in question is produced on each occurrence of the reaction in question; if two or more such molecules are produced, the corresponding digit is inserted. Similarly, -_1_ indicates that

Table 4-17. ILLUSTRATION OF MATRIX METHOD OF FORMULATING REACTION RATE EQUATION

(Mechanism by Shepp[71] for photolysis of acetone)

$CH_3COCH_3 + h\nu \longrightarrow CH_3CO + CH_3$ $\qquad \varphi I_a = k'_1$

$CH_3CO \longrightarrow CH_3 + CO$ $\qquad k_2$

$CH_3 + CH_3COCH_3 \longrightarrow CH_4 + CH_2COCH_3$ $\qquad k_3$

$CH_3 + CH_2COCH_3 \longrightarrow C_2H_5COCH_3$ $\qquad k_4$

$CH_3 + CH_3 \longrightarrow C_2H_6$ $\qquad k_5$

Let component 1 = CH_3COCH_3, 2 = CH_3CO, 3 = CH_3, 4 = CO, 5 = CH_4, 6 = CH_2COCH_3, 7 = $C_2H_5COCH_3$, 8 = C_2H_6

Reaction Number	System Components							
	1	2	3	4	5	6	7	8
1	-1	1	1	0	0	0	0	0
2	0	-1	1	1	0	0	0	0
3	-1	0	-1	0	1	1	0	0
4	0	0	-1	0	0	-1	1	0
5	0	0	-2	0	0	0	0	1

$r_1 = dC_1/dt = -R_1 - R_3 = -k'_1 C_1 - k_3 C_1 C_3$

$r_2 = dC_2/dt = R_1 - R_2 = k_1' C_1 - k_2 C_2$

$r_3 = dC_3/dt = R_1 + R_2 - R_3 - R_4 - 2R_5 = k_1' C_1 + k_2 C_2 - k_3 C_1 C_3 - k_4 C_3 C_6 - 2k_5 C_3^2$

Table 4-17. ILLUSTRATION OF MATRIX METHOD OF FORMULATING REACTION RATE EQUATION

$r_4 = dC_4/dt = R_2 = k_2C_2$

$r_5 = dC_5/dt = R_3 = k_3C_1C_3$

$r_6 = dC_6/dt = R_3 - R_4 = k_3C_1C_3 - k_4C_3C_6$

$r_7 = dC_7/dt = R_4 = k_4C_3C_6$

$r_8 = dC_8/dt = R_5 = k_5C_3^2$

one molecule is consumed, and -2 that two molecules are consumed on each occurrence of the given elementary reaction step.

From the matrix (Table 4-17) the expressions for the rates of the elementary reactions are formulated by reading the corresponding row to identify the reacting components (corresponding to the columns containing negative stoichiometric coefficients), then multiplying their concentrations, each raised to the appropriate power, together with the rate constant for the reaction. The rate of change of concentration of each component is then formulated by reading down the appropriate column for non-zero entries and adding the individual rates of the indicated reactions, each multiplied by the indicated stoichiometric coefficient (including the sign).

Mathematically this process can be expressed as

$$R_j = \prod_{i=1}^{m} (S'_{ij}\ C_i)^{S'_{ij}}\ ,\ j=1,\ldots n \qquad (4\text{-}62)$$

where

$$S'_{ij} = |S_{ij}| \text{ if } S_{ij} < 0, \tag{4-63}$$

$$S'_{ij} = 0 \quad \text{ if } S_{ij} \geq 0. \tag{4-64}$$

and

$$r_i = (dC_i/dt) = \sum_{j=1}^{n} S_{ij} R_j, \ i=1, \ldots m. \tag{4-65}$$

In these expressions R_j is the instantaneous rate of the jth elementary reaction, while r_i is the net instantaneous rate of production of the ith component; C_i is the concentration of the ith component, and S_{ij} is the stoichiometric coefficient for component i in reaction j. S'_{ij}, as defined in equations (4-63) and (4-64) is the absolute value of S_{ij} for components consumed by the reaction only.

In principle, the procedure within the computer is to calculate the rates of change of all components, use these rates to estimate the expected changes of concentration during a specified minute interval of simulated time, then accordingly increment each of the concentrations previously calculated (or specified as input). This procedure is then repeated as often as necessary to reach the total desired simulated time. In practice it is necessary, however, to apply all possible simplifications and aggregations in the computation routine, to reduce computation time and cost, consistent with reasonable accuracy in the output.

3. Acceptable Simplifications

Some of the standard simplifications used in chemical kinetics in deriving the mathematical consequences of assumed chemical mechanisms are also useful in abridging the necessary input, output, or computations required in computer simulation.

a. Approximate Constancy of Concentration of Components Present in Large Excess.

The primary example of a component present in large excess in the atmospheric photochemical system is molecular oxygen, with a concentration near 200,000 ppm. Even high concentrations of hydrocarbons in the ambient atmosphere, say 20 ppm as carbon, if completely converted to carbon dioxide and water, would consume far less than one thousandth of the oxygen available. Thus the concentration of oxygen cannot change appreciably due to photochemical reactions, and it may be treated as a constant factor in those elementary reactions in which it occurs. For example, in the case of the reaction

$$2NO + O_2 = 2NO_2, \qquad (4\text{-}66)$$

the regular rate expression is

$$R = k\ (NO)^2(O_2). \qquad (4\text{-}67)$$

Assimilating the essentially constant value of (O_2) into the rate constant by the device

$$k' = k(O_2), \qquad (4\text{-}68)$$

the rate of the elementary reaction can be more briefly expressed as

$$R = k'(NO)^2. \qquad (4\text{-}69)$$

The same considerations can be applied to recombination reactions of atoms and small radicals, where a third molecule is necessary to carry away the excess energy; for example,

$$2OH + M = H_2O_2 + M \tag{4-70}$$

In this case, the formal rate expression is

$$R = k\ (OH)^2(M) \tag{4-71}$$

where (M) is the concentration of all unreactive molecules in the system. Here the rate is more simply expressed as

$$R = k'\ (OH)^2, \tag{4-72}$$

where

$$k' = k(M). \tag{4-73}$$

Since it is of little interest to compute the relatively minute changes of concentration of oxygen, water vapor and carbon dioxide which occur as the photochemical reactions proceed, these substances may be omitted from the list of components in the reaction matrix, provided that appropriate pseudo constants are calculated for the reaction steps which involve them.

b. Steady State Concentrations for Extremely Short-Lived Species

Free radicals, atoms, and various other highly reactive molecular species tend to be consumed so rapidly after they are formed that their average period of intact existence is very short. More importantly, under these conditions their concentrations remain always negligible relative to the concentrations of the less reactive primary contaminants. They remain, in most cases, so low that ordinary experimental methods fail to detect them;

yet, at the same time, the reactions in which they are produced and consumed may proceed as rapidly as, or more rapidly than, the reactions of the less reactive components.

To simplify the computations involving these species, whose exact concentrations in any event have yet to be experimentally tested, the principle approximation used in standard kinetic analysis is that of the "pseudo-steady state." It is assumed that the rates of change of concentration of such species are negligible. Then the concentration of each such component can be derived from the rates of the individual steps. In fact, it is found by dividing the total rate of production by the total relative rate of consumption. Mathematically, the rate of production of component i is

$$r_{pi} = \sum_{j=1}^{n} S''_{ij} R_j, \qquad (4\text{-}74)$$

where

$$S''_{ij} = S_{ij} \text{ if } S_{ij} > 0, \qquad (4\text{-}75)$$

$$S''_{ij} = 0 \quad \text{if } S_{ij} \le 0. \qquad (4\text{-}76)$$

The rate of consumption is

$$r_{ci} = \sum_{j=1}^{n} S'_{ij} Rj, \qquad (4\text{-}77)$$

with S'_{ij} defined as above (Equation 4-63) and 4-64), while the relative rate of consumption is

$$r_{ri} = r_{ci}/C_i = \sum_{j=1}^{n} (\prod_{k=1}^{m} (S'_{kj}\ C_k)^{S'_{ki}})/C_i. \tag{4-78}$$

Thus the approximate value of the desired concentration is

$$C_i = r_{pi}/r_{ri}. \tag{4-79}$$

c. Aggregation of Free Radical Termination Steps

Since free radicals, when they recombine, cause termination of radical chains, the aggregate effect of such steps may have an important effect on chain lengths and, thus, on rates of product formation. However, the absolute rates of these reactions are relatively small because of the very low concentrations of the radicals; hence the formation of recombination products is not important relative to other routes of product formation. To avoid expanding the reaction set to include a large number of recombination reactions, it is convenient to assume that all such reactions have the same rate constant, and thus aggregate the corresponding elementary rate terms into a single term for each listed free-radical component.

4. Photo-oxidation Simulations

Mechanisms of the type discussed here have been successfully utilized in digital computer simulation of photo-oxidation kinetics by Wayne and Ernest[72] and by Westberg and Cohen[73]. In the first example, a list of forty proposed elementary reactions served as the hypothetical mechanism, involving as initial reactants three species (nitrogen dioxide, nitric oxide and propylene) in addition to atmospheric oxygen; nine products, in addition to carbon dioxide and water; and fifteen intermediate species, mainly free radicals. This list of reactions is shown in Table 4-18.

For these forty reactions, rate constants were either taken from the literature or estimated on the basis of modern methods in chemical kinetics The degree of success attained in simulating, with this mechanism, several experiments in the photo-oxidation of propylene, is illustrated in Figure 4-5. and Table 4-19. Even without any substantial effort at fine tuning, all simulated concentrations were within 20 percent of the experimental points, not only for the species shown in the figure, but also for the aldehydes produced by the photo-oxidation.

Table 4-18. 40-STEP MECHANISM FOR PHOTO-OXIDATION OF PROPYLENE

(27 participating species underlined, excluding O_2, H_2O, CO_2)

1. $\underline{NO_2} + h\nu \longrightarrow \underline{NO} + \underline{O}$
2. $O + O_2 + M \longrightarrow \underline{O_3} + M$
3. $O_3 + NO \longrightarrow NO_2 + O_2$
4. $2NO + O_2 \longrightarrow 2NO_2$
5. $NO_2 + O_3 \longrightarrow \underline{NO_3} + O_2$
6. $NO_3 + NO_2 \longrightarrow \underline{N_2O_5}$
7. $NO_3 + NO \longrightarrow 2NO_2$
8. $NO + \underline{HO_2} \longrightarrow NO_2 + \underline{OH}$
9. $\underline{C_2H_3O_3} + NO \longrightarrow \underline{C_2H_3O_2} + NO_2$
10. $C_2H_3O_2 + NO \longrightarrow \underline{C_2H_3O} + NO_2$
11. $\underline{CH_3O} + NO \longrightarrow \underline{CH_3} + NO_2$
12. $\underline{CH_3O_3} + NO \longrightarrow \underline{CH_3O_2} + NO_2$
13. $CH_3O_2 + NO \longrightarrow CH_3O + NO_2$
14. $\underline{C_2H_4O_2} + NO \longrightarrow \underline{CH_3CHO} + NO_2$
15. $CH_3O + O_2 + NO \longrightarrow CH_3O_2 + NO_2$
16. $CH_3 + NO_2 \longrightarrow CH_3O + NO$
17. $CH_3O_2 + NO_2 \longrightarrow NO + O_3 + CH_3$
18. $O + \underline{C_3H_6} \longrightarrow CH_3 + C_2H_3O$
19. $O_3 + C_3H_6 \longrightarrow \underline{HCHO} + C_2H_4O_2$
20. $CH_3O + C_3H_6 \longrightarrow 2CH_3 + C_2H_3O$

Table 4-18. 40-STEP MECHANISM FOR PHOTO-OXIDATION OF PROPYLENE (continued)

(27 participating species underlined, excluding
O_2, H_2O, CO_2)

21. $CH_3O_2 + C_3H_6 \longrightarrow CH_3 + CH_3O + C_2H_3O$
22. $C_2H_3O_2 \longrightarrow HCHO + \underline{CHO}$
23. $C_2H_3O + O_2 \longrightarrow C_2H_3O_3$
24. $CH_3 + O_2 + M \longrightarrow CH_3O_2 + M$
25. $C_2H_3O + OH \longrightarrow CH_3CHO + O$
26. $CH_3O_2 + O_2 \longrightarrow O_3 + CH_3O$
27. $O + HCHO \longrightarrow OH + CHO$
28. $O + CHO \longrightarrow \underline{CO} + OH$
29. $OH + CHO \longrightarrow CO + H_2O$
30. $CH_3CHO + OH \longrightarrow CH_3CO + H_2O$
31. $2CH_3CO \longrightarrow CH_3CHO + \underline{C_2H_2O}$
32. $CH_3O + O_2 \longrightarrow CH_3O_3$
33. $CH_3O + O_2 \longrightarrow HCHO + HO_2$
34. $\underline{H} + O_2 \longrightarrow HO_2$
35. $CO + OH \longrightarrow H + CO_2$
36. $2OH \longrightarrow O + H_2O$
37. $CH_3O + NO_2 \longrightarrow \underline{CH_3ONO_2}$
38. $C_2H_3O_3 + NO_2 \longrightarrow \underline{C_2H_3O_3NO_2}$
39. $CH_3 + NO_2 \longrightarrow \underline{CH_3ONO}$
40. $CH_3 + NO \longrightarrow \underline{CH_3NO}$

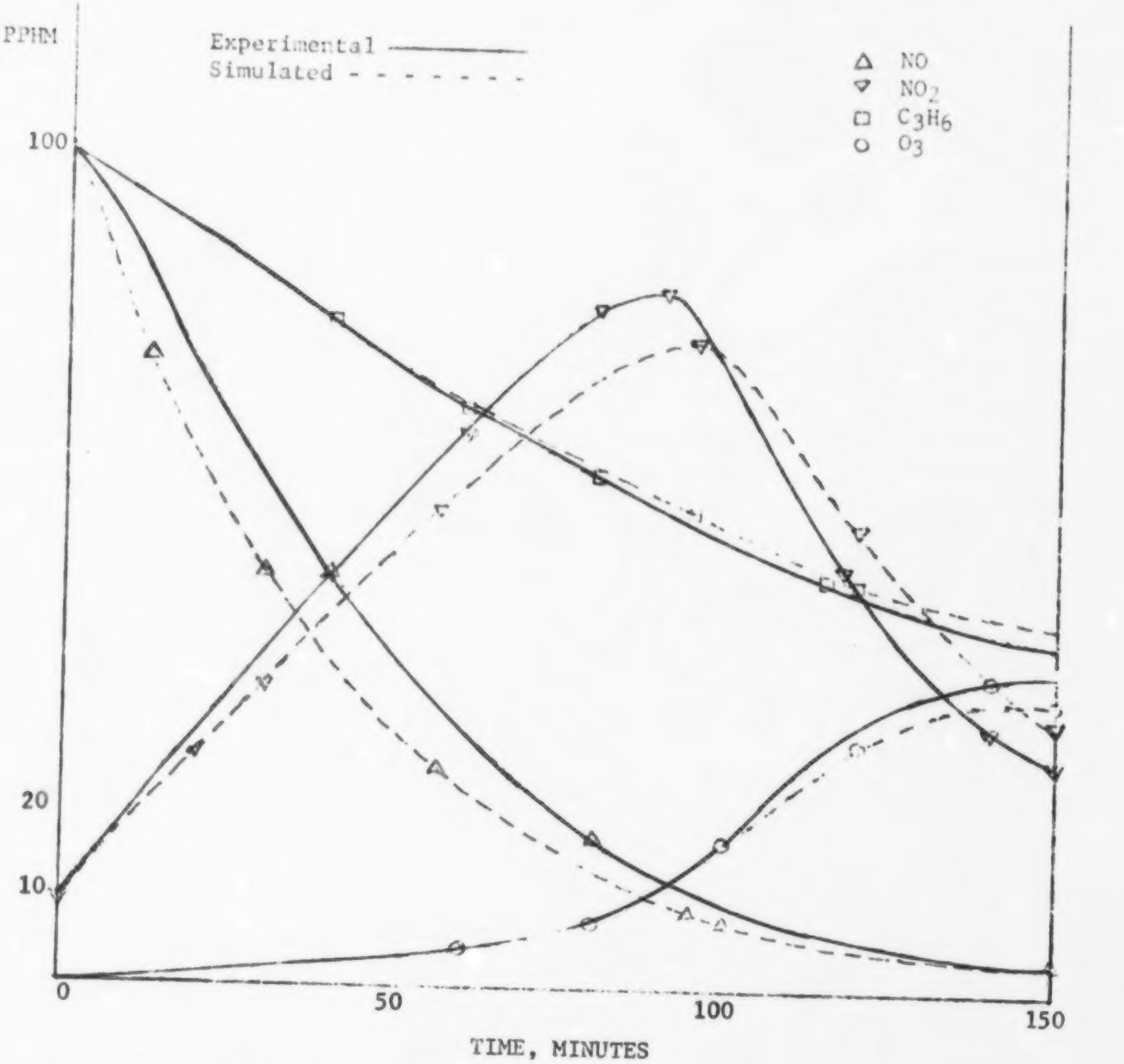


Figure 4-5. TIME-DEPENIENCE OF CONCENTRATIONS IN SIMULATED PHOTO-OXIDATION OF PROPYLENE FOR 40-STEP MECHANISM, COMPARED TO EXPERIMENT

Source: Wayne and Ernest.[72]

Table 4-19. COMPARISON OF SIMULATED RESULTS WITH EXPERIMENTAL PHOTO-OXIDATION RUNS

Initial Concentrations, pphm				Maxima, pphm			Half-time, minutes	
HC	NO	NO_2		NO_2	O_3	CH_2O	NO	C_3H_6
100	100	10	sim.	79	35	44	30	115
			exp.	85	37	48	40	115
100	100	2	sim.	72	35	44	30	115
		(10)	exp.	85	37	48	40	115
200	100	10	sim.	79	42	85	25	90
			exp.	80	45	80	30	95
100	200	10	sim.	140	26	38	63	145
			exp.	150	30	40	80	150

A similar degree of success has been reported by Westberg and Cohen[73] in simulating the kinetics of photo-oxidation as measured in an experiment by Schuck and Doyle.[70] The comparison of measured and calculated rates for several components of the system is shown in Figure 4-6. The mechanism as presented by the authors comprises 42 equations, but since several of these represent general reactions of a series of radicals, the total number of reactions involved is 68, with more than 40 participating species.

Exploration of the effects of variations in the rate parameters which were subject to estimation showed only four to which the simulated rates were significantly sensitive. These were as follows:

$$RO_2\cdot + NO = RO. + NO_2$$

$$HO_2\cdot + RO_2\cdot = ROOH + O_2$$

$$(CH_3CO)O_2 + NO_2 = (CH_3CO)OONO_2$$

$$\begin{aligned} C_4H_8O_3 &= (CH_3)_2CO + H_2CO_2{}^* \\ &= CH_2O + (CH_3)_2CO_2{}^* \end{aligned}$$

(As between the last two of these reactions, only the ratio of the rates was significant.)

The calculations further indicated a strong possibility that carbon monoxide could play an important role in converting nitric oxide to nitrogen dioxide and in generating ozone in a polluted atmosphere.

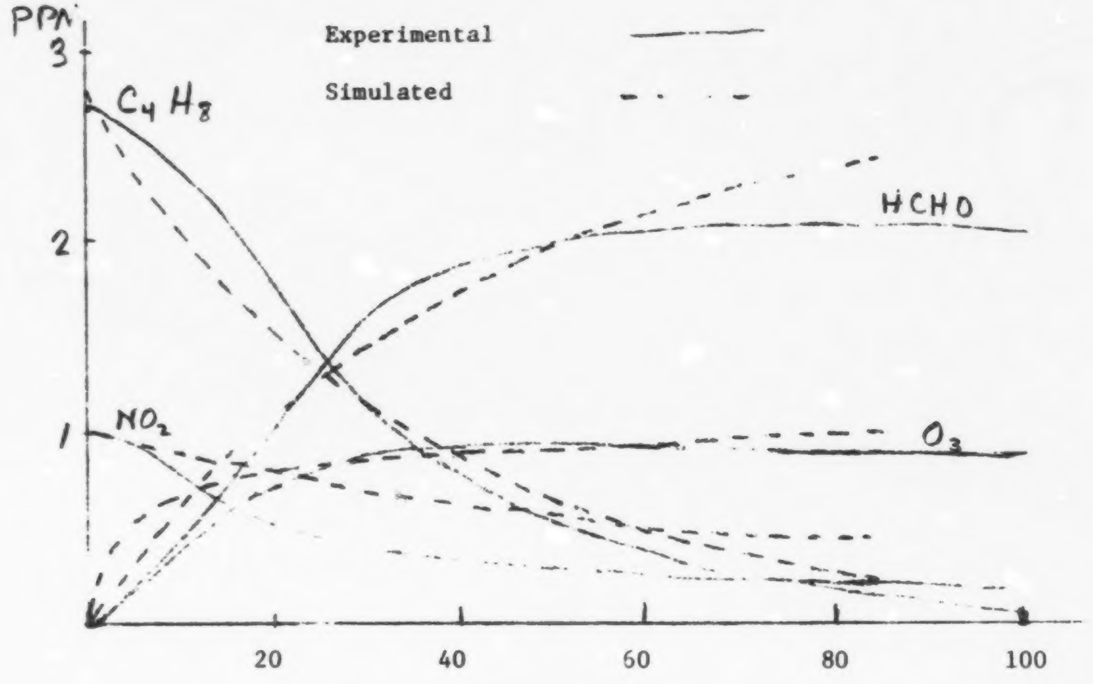


Figure 4-6. TIME-DEPENDENCE OF CONCENTRATIONS IN SIMULATED PHOTO-OXIDATION OF ISOBUTENE, COMPARED TO EXPERIMENT. FROM CURVES PRESENTED BY WESTBERG AND COHEN.[73]

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A. INTRODUCTION

Air quality appraisal consists of the measurement of contaminants in the atmospheric photochemical pollution system and/or their indicators to assess temporal and spatial air quality profiles in a given region. Measurement of air quality is constrained by costs and technical feasibility in terms of the design, performance and geographical deployment of sensors, operational and maintenance requirements and the representative sampling that may be required to give valid results in any region. Because of these considerations, an "optimized," i.e., cost-effective, strategy to appraise photochemical (as well as nonphotochemical) air quality is required. The considerations involved in the development of an implementation plan are discussed in paragraphs J. and K. of this chapter.

A cost-effective air quality appraisal plan is based, initially, on an analysis of current and prospective technical requirements, and costs and benefits are compared in order to select the sensors and sensor systems that are most preferred in meeting these requirements. An optimum plan would probably lead to applying measurements to carefully selected key contaminants which, when coupled with the measurement of selected environmental parameters (winds, mixing height, solar radiation), yield the greatest amount of interpretive information and the greatest degree of verification and predictability within the resources available.

The interaction of numerous reactants under irradiation in the photochemical system leads to a large number of intermediates and products, many of which are themselves capable of entering into the reaction sequence to some degree. Even in the most simplified synthetic smog systems the estimation of concentrations of all products as they vary with time has been an immense task. Only certain components can be practically measured in the atmosphere, some of these with great effort. Nevertheless, this assay is possible and is necessary to show clearly the nature of any given photochemical air pollution system. Suitable techniques for estimating the concentrations of contaminants in terms of the state-of-the-art and current consensus are described in the following paragraphs.

B. GENERAL SAMPLING AND STANDARDIZATION METHODS

The data necessary to determine the air quality in a region should be adequate enough to cover the region spatially and frequent enough over sufficiently protracted time periods to show normal fluctuations. The number of observations that may be required, therefore, is large enough to make automatic analysis preferable to manual, where available. Although automatic equipment is more expensive initially, its much lower requirements in man-hours per sample period soon compensate for initial costs. Manual methods are still needed, however, for (1) calibration, (2) management of special short-term sampling problems, and (3) situations in which automatic methods exist. These problems have been recently reviewed.[1]

Sampling an air pollutant usually involves moving a measured amount of air through or into a scrubber or collector. The inlet tube is sized according to flow rate and must not absorb or react with the pollutant to be measured. Usually glass, stainless steel or certain plastics such as polyethylene or Teflon are used, depending on the pollutant. In a grouping of several analyzers, a common manifold with a tube to each analyzer is customary. The air is moved by means of a pump. To avoid contamination by pump oil or other pump components, a vacuum pump is ordinarily placed downstream from the collector. If the pump must be used upstream with positive pressure, it should be of a type in which components coming into contact with the sample are inert towards the pollutant.

Measurement of the sample is done either by timing the flow at a measured flow rate or by measuring the total sample volume. Flows are conveniently measured by pressure drop across a constriction in the inlet (such as a capillary, hypodermic needle,[2] or nozzle) or by a rotameter. Either of these types should be calibrated against a volume-measuring device such as a wet or dry test meter, and the flow checked frequently for steadiness during the sampling period. Automatic analyzers with liquid reagents also require steady flow in one or more liquid streams, usually gauged with rotameters.

Calibration at periodic intervals is required for either manual or automatic methods. It may be dynamic or static. Dynamic calibration involves passing the pollutant in air into the system at realistic concentrations as if it were an actual sample. This may be fairly difficult because of the very low concentrations of pollutants, and the reactivity or condensability of some of them. Specific cases are discussed below as they arise.

Various gas dilution systems have been described.[3] A fairly simple method recently developed is the permeation tube,[4] suitable for pollutants which may be passed through the walls of a tube of a specific plastic at a slow rate which depends on the surface area and the temperature. To generate a known dynamic concentration, air is passed over the tube in a thermostatted vessel. The tube may be calibrated gravimetrically if held at constant temperature, and the permeation rate remains constant as long as appreciable liquid remains inside. Another technique is to add a measured amount of pollutant to a known fixed volume of air in a large vessel. The addition may be made by syringe injection or by crushing a weighed glass ampoule containing the pollutant. If the vessel is rigid it must be large relative to the amount of sample to be withdrawn. Bags made of plastics such as Mylar or Tedlar[5] may be used for this purpose, and have the advantage of collapsing as the sample is withdrawn.

In static calibration a standard solution of the pollutant, a substance which will generate the pollutant, or the final reaction product may be used. Quantitative dilutions to various levels are made and the appropriate later stages of the determination are made, omitting the gas-contacting step. Static methods are inherently capable of better control and precision than dynamic methods, but give no indication of gas absorption or reaction efficiencies. Occasionally samples must be returned to a central laboratory for analysis. The form in which they are transported must be chosen so that they do not deteriorate in storage or transit. Some may be absorbed in the appropriate reagent, others must be kept in gas form. For the latter purpose, evacuated glass vessels or plastic bags are sometimes used.[5]

For condensable pollutants a freeze-out technique may be used. The air is passed through a trap immersed in a cold bath (ice, dry ice, or liquid air) suitable for condensing the materials of interest. Sometimes the trap is packed with an inert solid absorbent. Later the trap is connected to the detector and warmed up to volatilize the sample. In this method the normal large quantities of water vapor in air also condense. The water can sometimes be removed by a drying agent if the pollutant of interest is not also affected as a result.

C. NON-NITROGENOUS OXIDANTS

1. "Net Oxidant" Concept

Total oxidants in air may be defined as compunds that will oxidize a reference material which is not capable of being oxidized by atmospheric oxygen. Methods which measure oxidants, therefore, involve exposing a reference substance to a sample of ambient air, and determining the degree of oxidation which has occurred. This is done in different ways, depending on the reference substance chosen. The following factors should be considered:

a. Ambient air contains a mixture of oxidizing and reducing compounds--ozone, nitrogen dioxide, peroxaycetyl nitrate (PAN), sulfur dioxide, hydrogen sulfide, aldehydes, unsaturated hydrocarbons, and others.

b. The concentrations of these compounds may be constantly varying within relatively wide limits--from 0-2 mg/m^3 (0-1 ppm as ozone).

Since reducing compounds in air have an opposite effect on the reference material--that is, a decrease in the degree of observed oxidation--the result obtained by potassium ioxide (KI) methods (see paragraph 3. below), unless empirical corrections are made, is a "net" oxidant value rather than a total one.[6] The net value thus describes a condition of the air, rather than a specific compound concentration. For this reason, concentrated efforts are being made by researchers to obtain measurements for each specific oxidant present. Hopefully, these efforts will enable air pollution scientists to better define this atmospheric "condition."

Most oxidant data which have been collected are net determinations, and a high correlation between these values and other pollutant levels has been observed.[7] Consequently, until the more promising methods become routinely available, "net" determinations must serve as indicators of total oxidant levels.

2. Standards

For dynamic calibration ozone may be generated in the air stream either by glow discharge or by irradiation with a germicidal ultraviolet lamp. Since neither method offers a precisely known ozone concentration, determination by manual absorption train is required.[8] Usually potassium iodide reagent is used and is assayed colorimetrically or by titration with thiosulfate. Electric discharge in air may produce some oxides of nitrogen. These should be measured by a separate method, since the oxidant method is sensitive to them. The influence of these contaminants can be negated by generating the ozone in a stream of pure oxygen instead of air. Figure 5-1 illustrates this procedure.

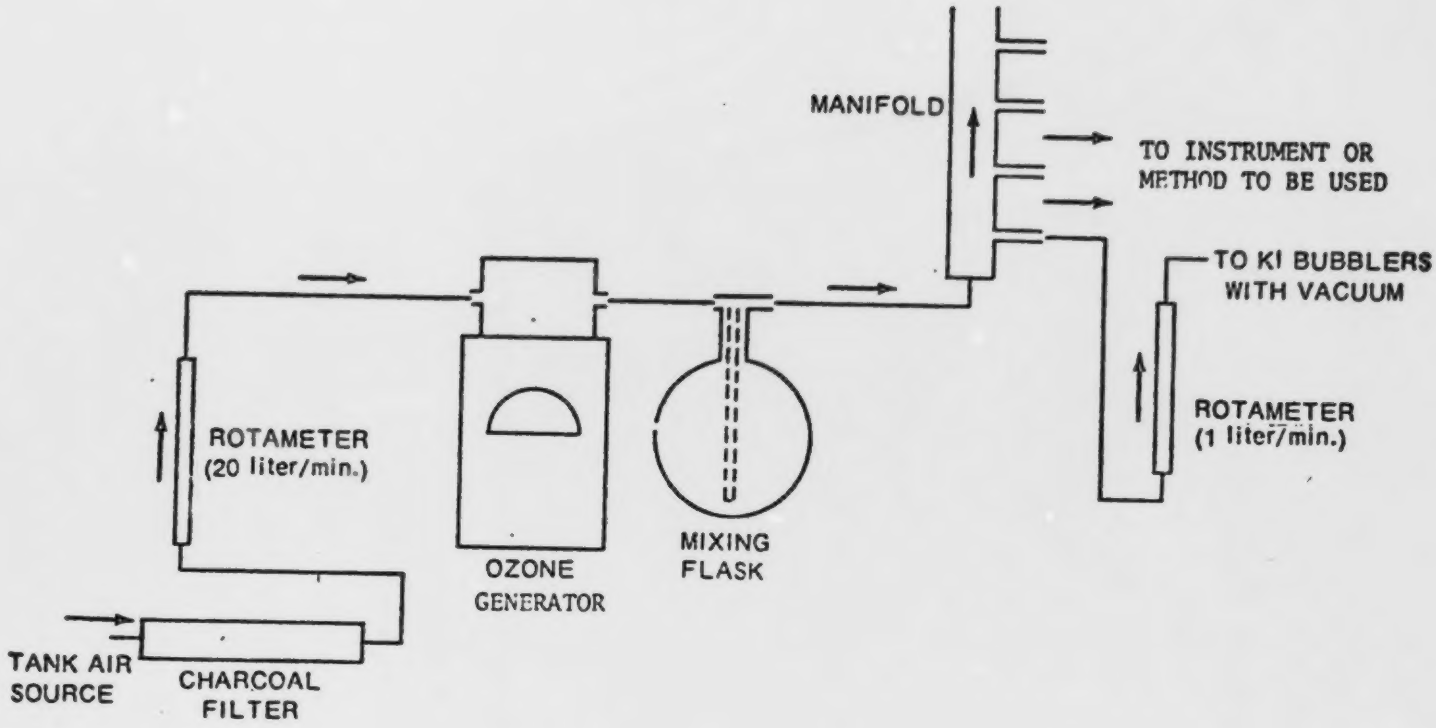


Figure 5-1. APPARATUS FOR DYNAMIC CALIBRATION.

Except for nitrogen dioxide and peroxyacyl nitrates, which are treated separately below, there is little experience in dynamic calibration with other oxidants. They are calibrated with static procedures. Hydrogen peroxide is available in reagent grade and may be standardized by conventional titrimetric methods. Certain other peroxides such as t-butylhydro-peroxide, di-t-butylperoxide, or peracetic acid are available in reasonable purity and are used to represent the whole class of their homologs, many of which are unstable and not readily available.

3. Total Oxidant Measurement Techniques

a. Colorimetric KI

Continuous analysis of total oxidants is most commonly accomplished with instrumentation using neutral buffered potassium iodide as the absorbing medium. In devices using a colorimetric method, sample air is passed at a known rate through a liquid-absorbing reagent with a vacuum pump arrangement. Oxidants in contact with the KI react to free iodine and the tri-iodine ion. These are determined colorimetrically in a continuous flow colorimeter at 352 mu. The continuous instrumental method is extremely sensitive to oxidizing substances and is suitable for determinations in the 0-05 ppm (0-1 mg O_3/m^3) range, with a sensitivity of about 0.005 ppm (.01mg/m^3) as ozone. The negative interference caused by SO_2 is often reduced by passing the air sample over CrO_3 scrubbers, but this technique has not been wholly successful, primarily because of the effects of humidity on the scrubber systems, oftentimes rendering them ineffective.[9] Better methods for eliminating SO_2 interference are critically needed.

b. Coulometric

In these devices, which are also widely used for measurement of oxidants, sample air is passed in a manner similar to the colorimetric type of instrument into an electrolytic detector cell containing potassium iodide.[10] The free iodine liberated by the oxidants is reduced at the cathode of the cell, causing a current flow through an external circuit. The current flow is proportional to the amount of iodine liberated and, in turn, to the oxidants entering the solutions. The current is measured with a microammeter usually calibrated directly in pphm or mg/m^3 of ozone.

c. Coulometric vs. Colorimetric Methods

Since these general types of instruments are the most widely used for oxidant measurements, numerous studies have been conducted comparing the results obtained with the two approaches. Field comparisons of colorimetric and coulometric oxidant analyzers indicate differences would be no greater than those of two colorimetric analyzers working side-by-side.[11] Comparative data show a correlation coefficient of 0.87 between readings of the two different instruments, both calibrated with respect to known ozone streams. In this study, however, this coefficient was the result of a least squares fit and in some instances, the agreement between the two methods was poor.

In another field study[12] the two methods agreed within their respective degrees of precision after correction for NO_2 responses.

Analyzers utilizing other principles of detection vary in their sensitivity to NO_2. As shown in Table 5-1, the coulometric cell analyzers

Table 5-1. EFFECT OF NO_2 OXIDANT DETERMINATION IN ABSENCE OF OZONE.

NO_2 Concentration Range Tested ppm* in air	Conditions	Response Percent of NO_2 Concentration	Reference
> 0 to 36	1% KI, pH 7 bubbler	8 to 11	13
1.5 to 5.5	2% KI, pH 7 bubbler	6.4	14
2.0	10% KI, pH 7 contact column	21	15
> 0 to 1	20% KI, pH 7 contact column	30	13
0.24 to 0.43	20% KI, pH 7 contact column	12 to 47 average: 25	16
2.0	coulombic cell	10	15
2.0	U. V. photometer	2	15

*Based on 4-liter sample,

register about 10 percent of the NO_2 concentration as ozone and the UV photometer device shows the least interference from NO_2.

Perhaps the largest variations between the methods are obtained because of the differences in reagent formulation. Generally, 10- or 20-percent KI solutions are used in colorimetric instruments, and at these concentrations, response to NO_2 is higher than at the 2- percent level used with coulometric instruments. Studies comparing the two methods indicate that both must be checked and calibrated often and that variations are usually caused by changes occurring in air or reagent flow, and by interfering compounds.

d. Other Methods

1) Alkaline KI

This method[13] is intended for the manual determination of oxidants in the range of a few pphm (mg/m^3) to about 20 ppm (40mg/m^3). The advantage of this procedure over the neutral iodide technique is that a delay between sampling and completion of analysis is allowed. Sampling is conducted in midget impingers containing 1 percent KI in 1 N sodium hydroxide. Because of the preferred reference neutral-buffered method, however, the alkaline procedure is not widely used.

2) Acid KI

This procedure was reported recently[17] to give good color stability, no SO_2 interference, and good agreement with results by neutral-buffered KI methods. It has not yet been widely tested.

3) Phenolphthalin

This method[18] is based on the oxidation of the colorless phenolphthalin to phenolphthalein, which is pink in alkaline solution by atmospheric oxidant. Because the method is sensitive to pH and temperature variation, it is no longer widely used.

4) Miscellaneous

The specificities of several colorimetric reagents to various oxidant species have been evaluated. They offer the means, when needed, for distinguishing among most of the oxidant classes to be expected in photochemical air pollution. Methods specific for ozone are discussed in the next paragraph.

D. SPECIFIC OZONE METHODS

1. Chemiluminescence

A chemiluminescent method originally developed by Regener for use in balloon sondes[19,20] has been adapted for use in surface measurements. A small pump aspirates air in the dark across the surface of a fluorescent substance (rhodamine B absorbed on silica gel) while the material is scanned with a photomultiplier tube. An inlet trap of desiccant eliminates moisture. The reaction is highly specific to ozone. Responses to NO_2, SO_2 and PAN appear to be negligible. However, the reaction is not stoichiometric and requires a timer to alternate flows of ambient air and clean air which has passed over a calibrated ultraviolet ozone generator lamp.

For several weeks the chemiluminescence method was compared[21] with colorimetric and coulometric KI analyzers in measurements on Los Angeles smog. It generally (but with some exceptions) read lower than the colorimetric analyzer. This very promising method is still being evaluated.

2. Rubber Cracking

The earliest technique used to identify ozone in ambient air was based on the rapid cracking of stressed rubber strips.[22] A strip of a suitable rubber is bent double, tied with a thread, and exposed to the air sample to be measured. Either the time until the rubber begins to crack or the degree of cracking after a specified time is then related to the ozone concentration. This procedure has the following advantages:

a. The equipment required is extremely simple.

b. The rubber is apparently sensitive only to ozone and not to other oxidants.

There are several disadvantages:

a. The simplicity of the equipment is offset by the necessity of calibrating the rubber and training the operator.

b. Continuous monitoring is extremely laborious.

3. Ultraviolet Photometry

Another method specific for ozone is based on ozone's absorption of ultraviolet lightwaves between the lengths of 3000 and 4000 A. Renzetti described an ultraviolet photometer using this band, and later a mercury vapor detector was developed.[23,24]

The strong mercury line at 2437A matches the peak absorption in the ozone band very closely. It is believed that there are no serious interferences.[15] The Kruger photometer was available commercially for several years. Because of electronic instability and temperature dependence, it required frequent attention and is not in extensive use.

4. Other Methods

A variety of oxidant and ozone methods were critically evaluated.[15, 24,51] Several spectrometric methods have been reported to be specific for ozone.[26,27,28,29] One of these involves ozone addition to 1,2-di-(4-pyridyl) ethylene.[28,29] There is one recent reference, one in which dihydroacridine is oxidized by ozone to acridine,[30] another in which N-phenyl-2-naphythylamine with o-dichlorobenzene gives a color with ozone.[31]

In a gas-titration technique[32,33] the incoming air is injected periodically with trans-2-butane, then held in a mixing chamber. This intermittent removal of ozone is quantitative and may be detected with a total oxidant analyzer such as the Mast detector. There is also a galvanic ozone method.[34] None of these methods has yet been used much in air monitoring.

E. OXIDES OF NITROGEN

1. Standards

The nitrogen oxides important in air pollution are nitric oxide, NO, and nitrogen dioxide, NO_2. Calibration with the relatively stable NO is made much as it is with other gases and only presents problems in that its oxidation at high concentrations in air is quite rapid.[35] (The rate for oxidation of NO to NO_2 by oxygen is proportional to the square of the NO concentration.) To avoid oxidation during dilution, one technique is to dilute it initially with nitrogen alone, then rapidly mix with air to the desired concentration. Once diluted to near atmospheric levels, the reaction is very slow. The fast oxidation may be used to advantage in some cases where small amounts of gaseous NO_2 are needed. Gaseous NO and a slight stoichiometric excess of air or oxygen are drawn successively into a gas-tight syringe, held for 30 to 60 seconds to complete NO_2 formation, then injected into the vessel where the NO_2 is wanted.[36]

Preparation of accurate low concentrations of NO_2 starting with the liquid is not a simple task, because at high concentration it tends to dimerize and condense in gas lines. The system must be heated beyond the point in the lines where adequate dilution has occurred. A precision gas dilution system,[37] an electrolysis system[38] and permeation tubes[4] have all been used for NO_2 dilution. One or another of these systems is needed for dynamic calibration. Static calibration is made with standard solutions of nitrite ion.

2. Colorimetric Methods

The Griess-Ilosvay reaction as modified by Saltzman[39] is the most popular method for determining NO_2. The NO_2 in acid solution in this reaction forms a colored dye complex with an aromatic sulfonic acid and an aromatic amine. There are numerous variations on this basic reaction. The method is used for both manual and automatic analysis and is quite sensitive (to 0.01

ppm NO_2, or better). By using an oxidation scrubber to convert it to NO_2, NO may also be determined.[40,41,42]

Although the original Saltzman reagent included sulfanilic acid and α-naphthylamine, the latter has been replaced by N-(1-naphthyl)-ethylenediamine hydrochloride. The medium is 14 percent (volume) acetic acid. (These reagents are used in the tentative method adopted by the Intersociety Committee on Methods for Ambient Air Sampling and Analysis.)[43] A similar formulation is used in automatic analyzers, where the coupled complex may be removed on a charcoal column and the reagent recirculated. Other variations are used.[1]

3. Other Methods

A gas chromatographic procedure exists for the analysis of NO and NO_2.[44] These contaminants possess characteristic infrared absorption patterns and with long path length optics may be assayed spectrometrically, although the NO absorption is rather weak. Remote-sensing correlation spectrometry, similar to that used for SO_2 determination,[45,46] has been applied to NO_2 detection and may be a useful procedure when fully tested. These and other remote sensing methods have been reviewed recently.[47]

F. GASEOUS ORGANIC POLLUTANTS

1. Total Hydrocarbons

a. Flame Ionization Analyzers

Originally developed as a detector for gas chromatography, the flame ionization technique was then adapted for total hydrocarbon analysis.[48] In this technique the increase in ion intensity upon introduction of a sample into a hydrogen flame is observed on an electrometer. The response is approximately in proportion to the number of organically bound carbon atoms in the sample. Carbon atoms bound to oxygen, nitrogen, or halogen give reduced or no response. There is no response to nitrogen, carbon monoxide, carbon dioxide, or water vapor, but there is an oxygen effect which can be minimized by appropriate operating conditions. The response is rapid and, with careful calibration, fairly sensitive (to a fraction of a ppm carbon, as methane). Some variations in response to various hydrocarbons occur. These must be accounted for in data evaluation.[49] The instrument also responds to hydrocarbon derivatives approximately according to the proportion of carbon atoms bound to carbon or hydrogen.

In typical polluted air samples the largest hydrocarbon component by far is methane, usually more abundant than all other hydrocarbons combined. Methane, however, is generally considered to be virtually inert in photochemical reactions. In effect, it serves as an inert dilutent, reducing the precision of reactive hydrocarbon measurement. This fact has led to attempts to measure methane and other hydrocarbons separately.[50] In one technique a carbon column is treated with methane until it "breaks through," i.e., no more methane is absorbed, although other hydrocarbons are still retained. This column, along with the flame ionization analyzer, constitutes a "methane only" analyzer. Run in parallel or in alternation with the conventional analysis, it affords a measure of methane and total hydrocarbons and, by difference, the nonmethane or close approximation of the reactive fraction.[51,52,53]

b. Spectroscopic Methods

These methods are usually applied to a sample concentrated by freeze-out or other technique. The principal problem is calibration. In many cases hexane is used as a calibration compound to represent the whole hydrocarbon class. In infrared methods the reading is made at about 3.4μ (the carbon-hydrogen bond stretch wavelength). This tends to give more weight to saturated hydrocarbons rich in carbon-hydrogen bonds than to unsaturates. If the absorbance at other infrared wavelengths can be read, some correction can be made for certain principal components such as methane, acetylene and ethylene.[1]

Nondispersive infrared instruments have similar limitations, although they may be calibrated with other hydrocarbon mixtures. For atmospheric analysis without freeze-out, the cell path lengths required are very long.[1]

2. Hydrocarbons by Type

a. Gas Chromatography

"GC" is almost the ideal method for atmospheric hydrocarbon analysis.[53,54] With flame ionization detection, it has sensitivity to the ppb range; with judicious choice of columns and temperatures, almost any desired separation of components can be effected. Its principal drawback is the lack of qualitative identification. This is usually alleviated by a standardized operation with both sample and reference materials, or by use of a qualitative detector such as an infrared or mass spectrometer to identify individual components.

For type separations with GC there are subtractive columns to be used before or after GC. Good examples are the mercuric perchlorate or silver sulfate-sulfuric acid columns which remove unsaturates and pass paraffins. This simplifies the total analysis problem where individual components of different hydrocarbon types overlap or interfere in the chromatogram.[53]

b. Spectrometric Method

Both infrared and mass spectrometric methods are capable of considerable discrimination among hydrocarbons, but their sensitivity levels necessitate a freeze-out or concentration step. Infrared spectra can show the proportions of various olefin types, the various aliphatic carbon-hydrogen types (primary, secondary or tertiary) and some aromatic types.[55] The mass spectrometer can differentiate paraffin, olefin plus naphthene, and aromatic groups, and in restricted narrow fractions may permit analysis for individual components.[56]

c. Miscellaneous Methods

A number of methods for olefin determination by colorimetric or coulometric techniques are available. The colorimetric reagents include phosphomolybdate[57] and p-dimethylaminobinzaldehyde in sulfuric acid.[58] Among various methods based on addition of bromine, a coulometric method based on time for bromine generation was used successfully in several studies.[59]

3. Oxygenated Gaseous Organic Methods

a. General Method

Only a few specific types of oxygenated organics have been shown to be present in the atmosphere, although others are strongly suspected. Except for one formaldehyde procedure,[60] there are no automated methods for these contaminants, only manual (mostly colorimetric). The contaminants definitely identified in the atmosphere include formaldehyde, other aldehydes, and formic acid. Ketones and alcohols are expected but not yet demonstrated. The methods for carbonyls are based largely on condensation reactions.[61] Sampling of oxygenates is difficult because of water solubility and ready condensation or adsorption in the system.

b. Bisulfite Method

This aqueous reagent forms moderately stable complexes with lower molecular weight aldehydes and methyl ketones.[62] Heavier aldehydes are too insoluble and ketones form unstable complexes. After complex formation the excess reagent is destroyed and the complex broken up. The released bifulfite is analyzed by iodimetry. The method is only moderately sensitive. The reagent is also used as a collection absorber for other methods because the carbonyls are readily liberated by acidification of the complex.

c. Other Condensation Reagents

There are numerous reagents in this class which will react with carbonyl compounds.[1] They include cyanide, hydroxylamine, phenyhydrazine, 2,4-dimitropheylhydrazine, Schiff's reagent,[60] 2-hydrazinobenzothiazole, 3-methyl-2-benzothiazole hydrozone (MBTH), and chromotropic acid.[63] The Schiff's reagent and chromotropic acid method are capable of good precision and sensitivity for formaldehyde when recent procedures are used. The MBTH is good for aliphatic aldehydes (including formaldehyde).[64,65,66,67] 2,4-dinitropheylhydrazine is one of the more nearly general carbonyl reagents,[68] since it reacts with both aldehydes and ketones; however, used colorimetrically there are shifts in wavelength with carbonyl type, and the gravimetric procedures are lengthy and insensitive for atmospheric work.

Formaldehyde has generally been found to be the predominant carbonyl compound found in the atmosphere. It is also water soluble and in most derivatives is not typical of the rest of its class. For this reason it is often desirable to use a specific procedure for formaldehyde (such as the chromotropic acid method),[63] then determine "total" aldehydes or carbonyls by another method and attempt to allow for the formaldehydes found independently.

The unsaturated aldehyde acrolein has also received special attention because, like formaldehyde, it is a known lachrymator found in measurable concentration in smoggy air. The method in common use employs 4-hexylresorcinol reagent and is specific and sensitive.[69] It is a colorimetric procedure.

There is still neither a general method which really measures "total" carbonyls for aldehydes completely nor a proven automatic analysis for any of them.

G. PEROXYACYL NITRATES

1. Long Path Infrared Spectroscopy

Peroxyacyl nitrates were discovered by means of long path IR,[70] but characterized several ways.[71] Several aliphatic homologs have been synthesized and show similar but not identical IR spectra.[72] The acetyl and propionyl compounds have been observed in the atmosphere.[73] The butyryl and benzoyl homologs have only been found by synthetic means, but the latter is reported to be an extremely potent lachrymator.[74] Peroxyacetyl nitrate is the most abundant in atmospheric samples thus far analyzed and is used for calibration. It has several characteristic absorption bands in the infrared which serve to identify and measure it.[72]

2. Gas Chromatography

Increased sensitivity for the detection of PAN is provided by gas chromatography using an electron capture detector.[75] The advantage of this detector is its relative insensitivity to other compounds which might interfere.

Short columns (9 to 18 inches by 1/8-inch diameter) packed with carbowax or an inert substance are used for the separation. Retention time for PAN is 1 to 2 minutes. Two ml samples containing 1 ppb of PAN give detectable peaks. A cycling automatic GC method has been described recently.[76]

H. AEROSOLS AND ATMOSPHERIC TURBIDITY

1. Particulate Collection Methods

a. General Properties of Photochemical Aerosols

In addition to the usual proportion of solid particulates (found even without a photochemical reaction system), the particulate material observed in a photochemical aerosol is partially liquid in character. There is generally a certain amount of moisture and other evaporable liquid present, which makes weight and volume estimates difficult and dependent on recent sample history. Prolonged passage of sample air over the aerosol may evaporate part of the collected material. The weight of a collected photochemical aerosol depends on the relative humidity in which it has been kept between collection and weighing.[77] The extent to which gaseous photochemical reaction products condense to liquid and perhaps solid materials, or condense into solid particulate material, is very uncertain. Thus aerosol collection, size separation, and characterization are still very difficult. Most of the conventional methods described below are collection methods which are suitable for solid particulates but have very uncertain effects on liquid aerosols. The methods based on light scattering do not affect the particles appreciably, but are hard to relate to known particulate sizes and densities.

b. Filtration

The ordinary fibrous filters are unsuitable for airborne particulates because the particles penetrate the filter and cannot be readily observed, counted, or sized. The preferred filter media are those which are not penetrated by the particles, e.g., membrane filters such as Millipore or Nuclepore. These are efficient collectors into which the particles penetrate little, and are available in a range of pore sizes suitable for collecting given size ranges of particles. Their pressure drops are generally not excessive. The membrane material may be selected so as to be soluble in chosen solvents, to allow suspension or solution of the collected material in a liquid for further assay.

c. Inertial Collection

This method directs the air sample stream against a solid surface at high velocity so as to adsorb particulates on the surface. Very small particulates require high air velocities, since otherwise they will follow the airstream paths and not settle on the solid surface. Impingement usually refers to the process as carried out within a liquid; impaction is a dry process. The cascade impactor uses several sequential impactions made to occur at serially increasing air velocities by reducing in steps the size of the jets or orifices through which the air flows towards the impaction surface. These collectors are suitable for particles down to about 1/3 to 1 micron in diameter. The Anderson Sampler[78,79] and the Lundgren Impactor[80] are examples of this type. The Anderson device has six to eight stages in which material is collected on flat dishes or plates. The size distribution at each stage has been accurately determined. In the Lundgren device, at each of four stages a slit faces a rotor covered with a collecting film or foil. Varying rotor speed allows for variable time resolution or collection density. These and other stage impaction devices are commercially available.

An example of centrifugal inertial collector is the Goetz Aerosol Spectrometer,[81] a device used mainly for research work. In it the air passes through a helical path against a rotating cone upon which particles are deposited in a graded mass sequence. The simpler cyclone is also a centrifugal collector but has no moving parts, using only the tangential velocity of the air stream. It is a simple, reliable device capable of many variations and moderate efficiency, but has been used more in industrial exhaust control than as an atmospheric analyzer.

d. Electrostatic Precipitation

This method is highly efficient for both solid and liquid particulates in the size range 0.01 to 10μ, but is limited by the stability of the particles at the operating temperature and the rate of gas flow. It is used more in industrial waste control than in atmospheric analysis. For further examination after collection the material must usually be transferred from the apparatus to another site, such as a microscopic slide. Commercial versions are available.[82]

e. Thermal Precipitation

The efficiency of this technique is very high for particles below 10μ, virtually 100 percent for particles below 5μ, both liquid and solid. Its limitation is principally the very slow rate of air flow and sample collection. It is particularly advantageous in not subjecting the particles to much force, so that they are collected without much alteration from their state in the gas phase. Commercial-sized units are available.[82]

2. In Situ Aerosol Analyzers

a. Photometric

In general, photometric methods require use of a light beam of wavelength that is an order of magnitude of the diameter of particles to be assayed.[82] With visible light, particles of about 0.2 to around 10μ are measurable. In one type of analyzer the light scattered at some selected angle by each particle is detected and counted to give an estimate of particle concentration.[83] If a pulse height analyzer is added, the particles may be counted in size ranges to determine the size distribution. In another type of system, used more in smoke or plume measurement, the attenuation of a standard light source is used to estimate the aerosol concentration.

A promising application of light-scattering by aerosols is the nephelometer of Charlson. In this device a photomultiplier detector at one end of a tube is shielded by fixed annual rings from direct view of a flashing xenon lamp at the side of the tube. Calibration is made with clean nitrogen (or even helium) for downscale readings, a series of heavier gases up to Freon 112 for higher molecular scattering levels, and a small fixed spot of reflective material behind a shutter for field calibration. The scattering intensities have been related to meteorological visibility estimates in a precise way.[85,86] The instrument is rugged and suitable for field use. A commercial version is under evaluation.

In the Lidar instrument[87] a tightly collimated beam of light (a laser is used) is flashed through the atmosphere. A telescope focused down the same path is used to collect back-scattered light for photomultiplier detection and display on an oscilloscope. There is a known intensity decay curve in clear air which is increased by scattering from any particulates. The time to any given response point can be related to the distance. Pointed upward, for instance, the presence of an inversion layer has been shown by discontinuities in the decay curve. The aerosol density may be estimated from scattering intensity.

b. Condensation Nuclei Counters

If submicron aerosol particles are present in an air sample in which the relative humidity is brought to supersaturation by adiabatic expansion, vapor condenses on the aerosol particles to give droplets detectable by optical methods. The expansion for any existing relative humidity may be varied so that aerosol particles of various size ranges are selectively effective in nucleation. The concentration of droplets under given conditions is a measure of aerosol concentration. Commerical instruments are available.[82]

I. BIOLOGICAL INDICATORS

1. Bacterial Response

Photochemical air pollution and some of its specific constituents have been shown to have bacteriostatic or bactericidal effects (in fact, ozone used as a germicide). The effects of gaseous smog components on bacteria apparently depend strongly on the medium in which the bacteria occur and possibly on the humidity. There have been efforts to use bacterial responses as smog indicators. In one example the bacteria were exposed to the impaction of photochemical aerosols, then growth inhibitation was estimated.[88] A more recent technique utilized luminescent bacteria.[89,90,91] The inhibitory effects of a synthetic smog on the luminescence was measured by a photodetector.

2. Plant Damage

Many types of plants are sensitive to photochemical air pollution. Plant damage is often the first indication of deteriorating air quality. Under laboratory conditions the types of damage to selected species are relatable to specific air pollutants. In ambient air, the damage is apt to be less readily diagnosed and it is suspected there are phytotoxicants in smog which have not yet been identified. The known agents include ozone, PAN and nitrogen dioxide.

3. Sensory Irritation

Photochemically polluted air usually has an odor--often described as pungent--somewhat akin to that of ozone itself at low concentrations. Heavily polluted air causes some people to feel discomfort in breathing, such as nose or throat irritation or chest pain. Probably the most universal irritation, however, is eye irritation.[92] In severe smog episodes a large fraction of those exposed suffer eye-smarting or burning, sometimes accompanied by lachrimation. Estimation of intensity or prevalence of eye irritation has been used as a smog indicator. The sensation is so subjective and variable among subjects that panels of at least five or six persons are ordinarily averaged. This makes the measurement clumsy and expensive as a routine measure.

J. AIR QUALITY DATA

The great bulk of available air quality data goes back little more than 15 years. In the middle 1950's, the Los Angeles County Air Pollution Control District (LACAPCD) established the first large-scale air monitoring network based upon the use of continuous automatic analyzers.[93] This network included potassium iodide oxidant records, Saltzman reagent dual nitric oxide and nitrogen dioxide analyzers, ozone photometers (for several years beginning in 1958) and, at a later date, flame ionization type hydrocarbon analyzers. At its peak this network comprised 14 stations.

In 1961, the State of California Department of Public Health organized a statewide cooperative air-monitroing network (SCAN) of 16 stations.[94] Six of these were equiped and operated entirely by the Department; the remaining nine were selected stations from the existing Los Angeles County network.

The Public Health Service opened the first station of its Continuous Air Monitoring Project (CAMP) in Cincinnati in October 1961.[95] By early 1962 five additional stations were opeating in Chicago, Philadelphia, San Francisco, New Orleans, and Washington, D.C., in cooperation with local air pollution control agencies. The station in New Orleans was moved to St. Louis in 1964, and in 1965 the San Francisco Station equipment was moved to Denver. Air monitoring in the San Francisco area was continued and expanded by the Bay Area Air Pollution Control District.

The Public Health Service has conducted numerous other air sampling activities, principally as a part of abatement or research efforts.[96] In the last few years there have been major expansions in monitoring efforts by local, State and Federal agencies. The cities of Chicago and New York, the Puget Sound area, the States of New Jersey, New York, and Pennsylvania have all embarked on such efforts incorporating telemetering capabilities. In California alone, oxidants are continuously measured at about 40 air monitoring stations. Many other local agencies, states and even industrial organizations and universities are engaged in programs that are almost daily adding to the available air quality data.

Air quality as related to the photochemical air pollution problem must be described in terms of a whole series of interrelated compounds. Some of these are of direct interest because of their effects on humans, animals, plants, materials, or visibility, and some because they are primary reactants which form substances responsible for the aforementioned effects. Several are or can be important from both points of view.

It is necessary then to present information on atmospheric concentrations for at least the most significant photochemical reactants and products. Of those compounds discussed earlier in this chapter, data are presented on total oxidant, ozone, nitrogen oxides, hydrocarbons, and PAN.

Even though substantial quantities of data are being collected, much of it is still relatively inaccessible. Substantial differences exist in reporting parameters, methods of data processing, computer software and hardware (where used) and hard copy output. In many cases collecting organizations are not equipped to provide substantial outside access to their data.

Most of the above problems are the result of rapid growth, changing demands on data format, and advancing technology, rather than lack of concern about the problems. National data banks have been proposed such as the Storage and Retrieval of Air Quality Data (SAROAD) system[97] of the Public Health Service. No single source exists, however, for even a major portion of the data collected nationally.

The contaminant data presented in this report are from the continuous air monitoring program (CAMP) stations and the New York-New Jersey Abatement project of the U.S. Public Health Service; several stations in California (two from Los Angeles area, one each from San Francisco and San Diego, one smaller coastal city, and one smaller inland city; Bayonne, New Jersey (State of New Jersey Network); New York City; Phoenix, Arizona; and, in the case of hydrocarbons and PAN, from special sampling activities of the USPHS, State of California, Los Angeles County APCD, and the University of California at Riverside.

1. Methods of Expressing Air Quality

The initial form of the basic contaminant data is dependent on the measuring system. This ranges from discrete samples taken over a given time interval to the record produced by a rapid response continuous analyzer. In either instance only a sample of the total atmosphere is available: and in the second, our continuous record still represents a single point in space.

The problem in selection of data reporting parameters is to provide sufficient information to enable drawing of inferences about the real and complete system and to judge the system against known criteria or standards relating to its effects. Figure 5-2 provides an example of the sampling results that might be obtained from the same system by three different approaches. Although the inference about the time of peak would be offset in the case of the grab samples, it is evident that 4-hour mean calculated from all three approaches would be very close.

Still other problems surround the task of relating distinct episodes to mean values over longer time periods. Here we first encounter "descriptive" statistics, or those used to determine position and dispersion. These statistics are useful in making comparisons among locations, seasons or years, and in describing the past or expected frequency of pollution events. A few of these common statistics are defined below.

The first is the arithmetic mean. This value is described as the sum of the observations divided by the total number of observations. If we let the n observations of some value x be denoted as $x_1, x_2, x_3, \ldots x_n$, and the mean as $\bar{x}$, then we can write the formula

$$\bar{x} = \frac{\sum_{i=1}^{n} x_i}{n}$$

where $\sum$ is the usual symbol for the sum of the values. A useful statistic describing the dispersion of these individual values is the variance, s^2, or the standard deviation, s. The variance is defined as the sum of the squares of the deviations from the mean, divided by one less than the number of observations. The formula expressing this value is

$$s^2 = \frac{\sum_{i=1}^{n} (x_i - \bar{x})^2}{n-1}$$

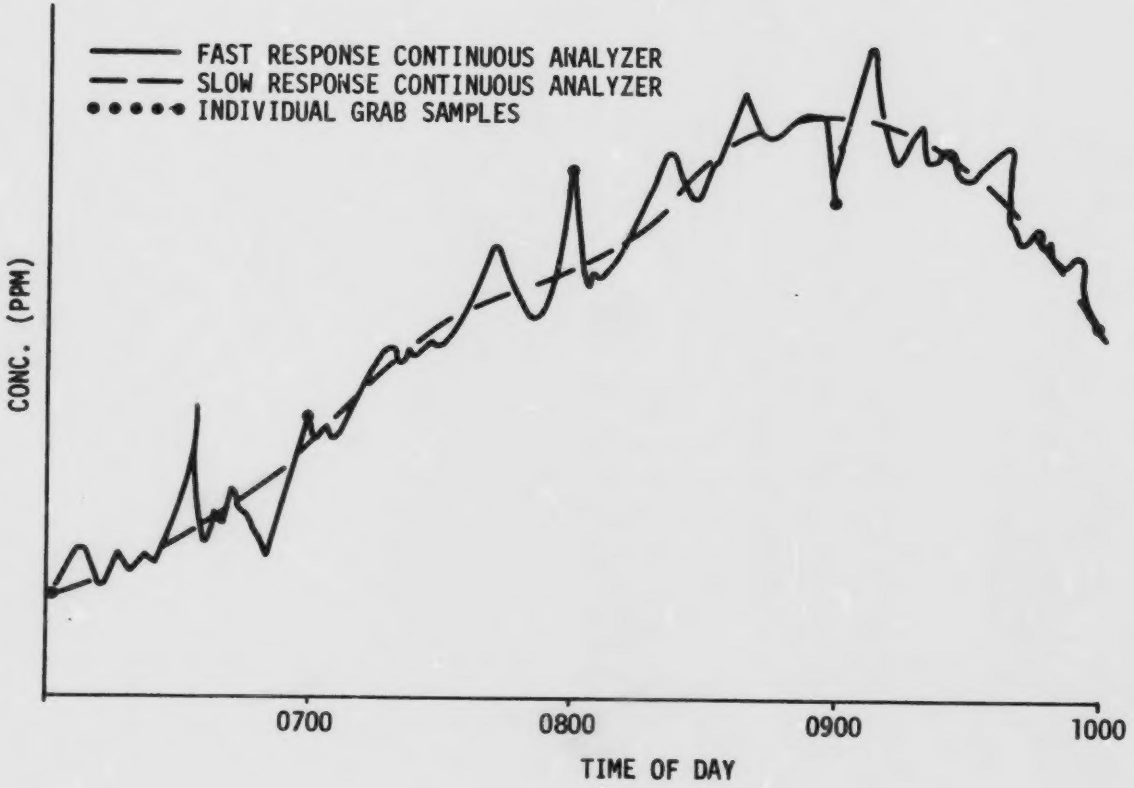


FIGURE 5-2. COMPARISON OF DATA RESULTING FROM THREE SAMPLING APPROACHES.

In some cases the distribution of a large number of values about the arithmetic mean is symmetrical. In these cases the distribution is described as "normal." In many situations in nature the distribution of the logarithms is normal. In these cases interest lies in the geometric mean illustrated somewhat indirectly in the formula below:

$$\log(\text{geometric mean}) = \frac{\sum_{i=1}^{n} \log x_i}{n}$$

where the logs are distributed normally, we have a "lognormal" distribution.

To illulstrate the effect of averaging, Figure 5-3 includes an hourly plot of the average oxidant values for 2 different days in a month, along with the mean monthly trace of these values. All are known as diurnal plots. The mean monthly curve is smoother than either of the other 2 days shown.

Although differences in data processing procedures and formats exist among the organizations collecting air quality data, there are several basic reporting parameters used by most for data acquired by continuous analyzers. These would include (1) peak concentration for each day (highest instantaneous value reached), (2) hourly average concentrations by each hour of the day, and (3) the maximum hourly concentration for each day. From these, basic day mean values over various time periods may be calculated and frequency distributions of the individual values or the means compiled.

Most organizations determine hourly average values by a simple graphical integration procedure using the recorder charts. In the U.S. Public Health Service CAMP network, the use of analog-to-digital converters

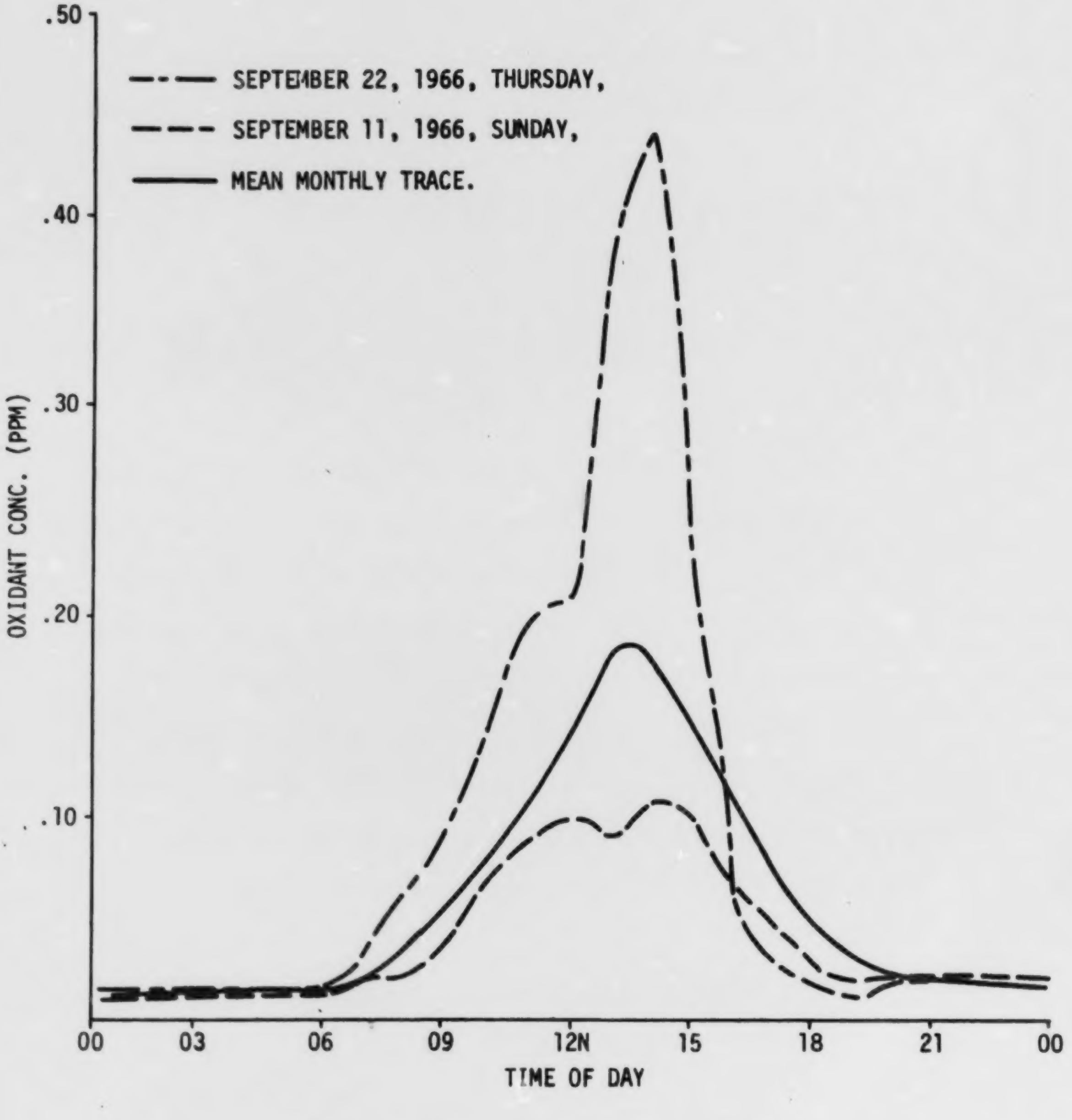


FIGURE 5-3. DIURNAL OXIDANT CONCENTRATIONS, POMONA, CALIFORNIA, SEPTEMBER 1966.

also provide machine-calculated or/ -machine determined hourly averages.

Most of the data presented in the remaining portion of this chapter deals with hourly averages as the basic unit of data. Those cases in which instantaneous values are used are clearly defined.

2. Typical Concentration Patterns in Photochemical Air Contaminants

In preparing an environmental appraisal of the photochemical air pollution problem, we must be concerned not only with specific time-concentration-frequency values for the individual contaminants for which effects criteria are available, but also with the interrelated temporal patterns exhibited by these substances. These patterns give form to the data and provide a preliminary insight into the character of the phenomena, i.e., possible differences resulting from location, from meteorological influences, and from emissions of air contaminants. More rigorous mathematical analyses and simulation modeling may extend or confirm this preliminary knowledge, but the visual impact of typical pollution patterns is an important first step in understanding the problem.

It is for this reason that most of the information on diurnal and seasonal variations in photochemical reactants and products is presented in the following subparagraphs. Furthermore, most information of this type is in graphical form. Hydrocarbon data are not generally included here because most such data from continuous analyzers provides only carbon atom concentrations with no separation of natural methane. Thus the patterns of reactive hydrocarbons are somewhat indistinct. Hydrocarbon data are discussed in section J4c.

a. Diurnal Variations

Inasmuch as air pollution is observed initially by incidents or episodes, Figure 5-4 is presented to show the diurnal variation of oxidant, nitric oxide, and nitrogen dioxide for a single day in the urban center of Los Angeles. The time of year is during the period that frequent photochemical air pollution episodes occur.

Before daylight, the primary contaminants NO, hydrocarbons, and CO remain fairly stable at concentrations somewhat higher than the daily minimums, which usually occur during daylight hours at times of maximum ventilation and mixing. NO_2 also fits the former pattern. Ozone is near zero. As human and traffic activity increase in the hours just after dawn, primary contaminants increase. As ultraviolet energy from the sun becomes available, nitric oxide peaks and nitrogen dioxide increases, often with a nearly complete conversion occurring. Finally, as the nitric oxide concentration (and thus the nitric oxide to nitrogen dioxide ratio) reaches very low levels, ozone begins to accumulate, reaching a peak about midday.

Before the ozone peak is reached, the primary contaminants and NO_2 normally have been declining for some time. Although not shown in this figure, other reaction products such as PAN peak at a time more closely corresponding with ozone than with the primary contaminants. In the usual situation, all contaminants decrease rather rapidly as the ventilation capacity of the atmosphere increases. This results from surface heating, which causes increased instability of the atmosphere, and from rising winds.

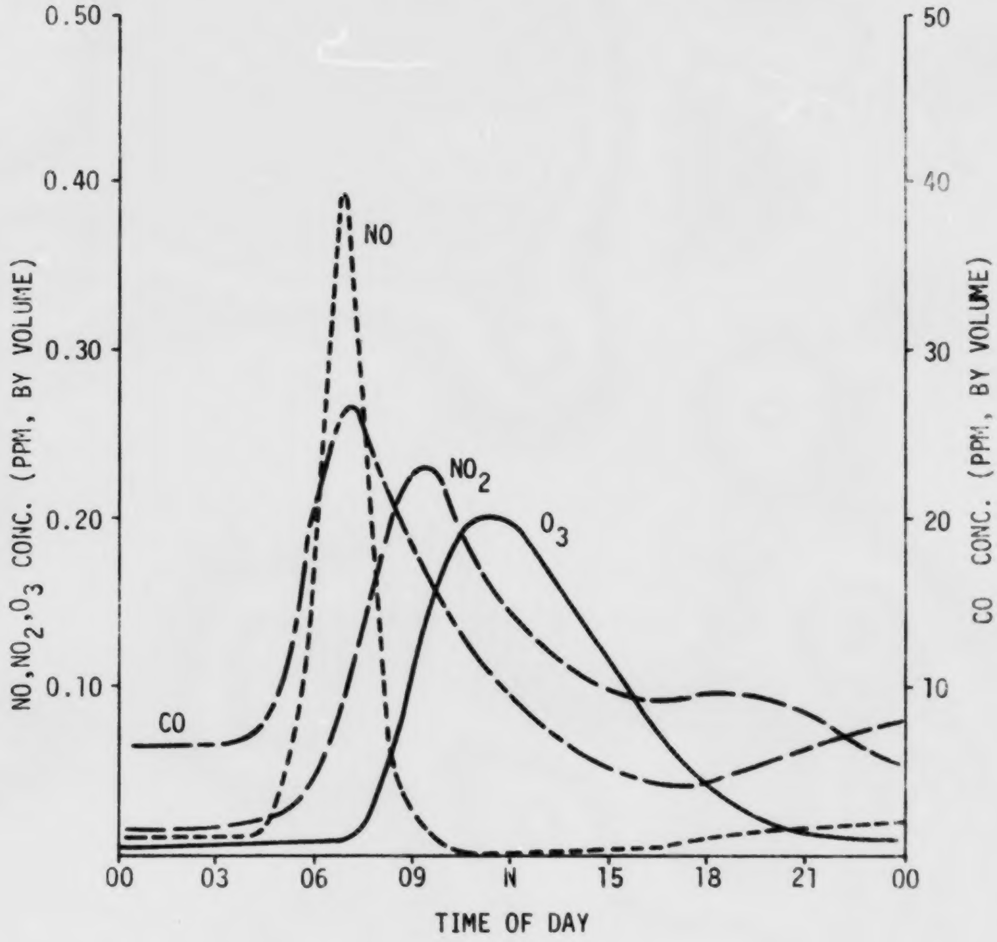


FIGURE 5-4. CONCENTRATIONS OF POLLUTANTS--LOS ANGELES, CALIFORNIA.

As solar intensity decreases, stability increases and winds decrease. The late afternoon and evening traffic increase results in increased concentrations of primary contaminants, but solar energy is no longer available to cause the photo-oxidation of nitric oxide and the production of ozone and other products.

It is obvious, but necessary, to point out that the concentration patterns shown in Figure 5-4 are for a single day at a single location. There are many factors which could result in absolute and relative levels of the concentrations and in their time distribution during the day. Of particular importance are (1) variations in time and nature of emissions of photochemical product-forming contaminatns, (2) variation in available solar irradiation and other photophysical variables, and (3) variations in transport and diffusion of contaminants in the atmosphere. All of the above influences may vary over very short time periods (hours), while the latter two categories also exhibit significant seasonal variations.

In general, the time of year having highest concentrations of oxidant and other photochemical products is between early summer and fall. If the zenith angle of the sun were the only consideration, the time of the summer solstice would produce the highest concentrations. However, periods of maximum atmospheric stability and low horizontal transport do not coincide in all locations of the country, thus producing a range in time of seasonal highs. The mean daily time of oxidant peak is near noon, although even here, cloud cover, thermal stability and the advection of pollutants may result in much later peaks or even in multiple peaks (commonly, two).

Figure 5-5 shows average diurnal traces for oxidant and NO_2 for Bayonne, New Jersey; Philadelphia, Pennsylvania; and St. Louis, Missouri. A peak oxidant month from the available data for each location was selected for this illustration. In each case the familiar pattern is followed: an early NO_2 peak, followed by an oxidant maximum near midday, and finally a late afternoon and evening rise in NO_2.

Figure 5-6 presents the diurnal variation in oxidant for Philadelphia on August 6, 1966 during a 3-day period (August 6-8) for which unusually high concentrations were observed. This illustrates the situation in which acute episodes in differing geographical locations can be quite similar, although the means show distinct differences. In fact, caution must be used in interpreting mean diurnal curves because statistical smoothing results in a trace which may not accurately represent any one single day. This is particularly true when comparisons with other contaminants are made. The ratio of means for any given period could likely be different from the mean of the individual ratios.

The specific time at which the oxidant value reaches its peak depends not only upon meteorological parameters governing accumulation and dispersion of the contaminants reacting to form this group of compounds (mainly ozone), but upon the spatial relationship of the point of measurement with the source area. To illustrate the effect of transport and source area, Figure 5-7 shows the monthly mean hourly average concentrations for October, 1965 for West Los Angeles, Los Angeles (center city), Azusa, and Riverside, California.

(BAYONNE, PHILADELPHIA, AND ST. LOUIS MONTHLY MEAN OF HOURLY AVERAGE CONCENTRATIONS.)

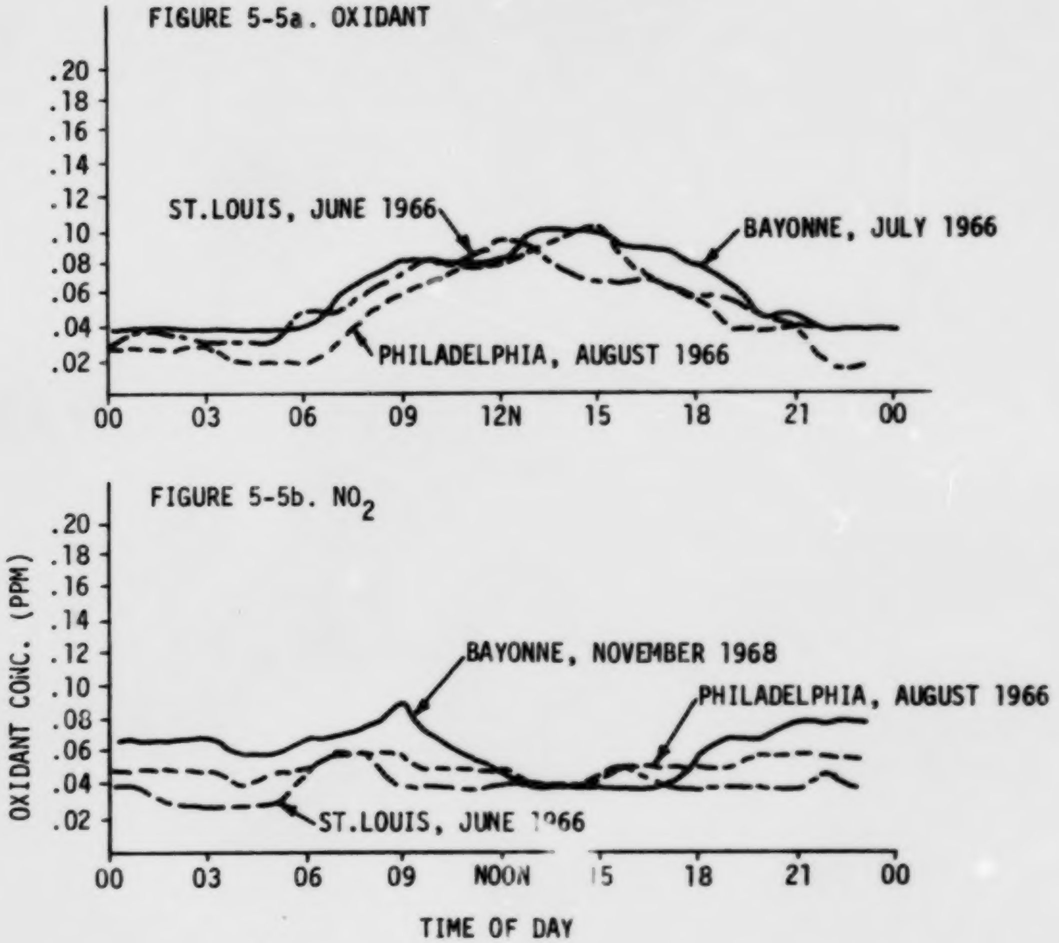


FIGURE 5-5. DIURNAL VARIATION IN OXIDANT AND NO_2 CONCENTRATIONS.

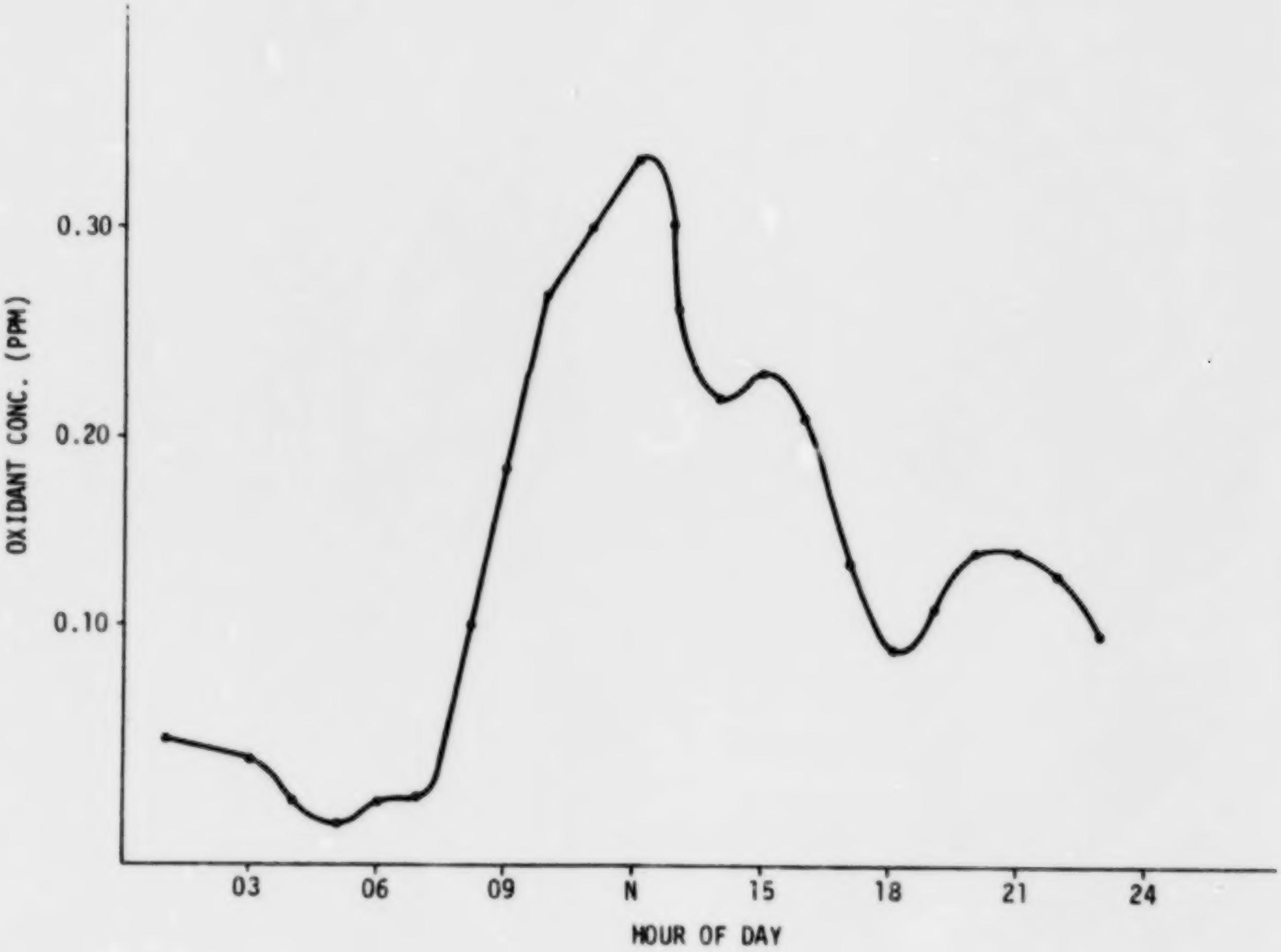


FIGURE 5-6. DIURNAL VARIATION OF TOTAL OXIDANT LEVELS--PHILADELPHIA, PENNSYLVANIA, AUGUST 6, 1966.

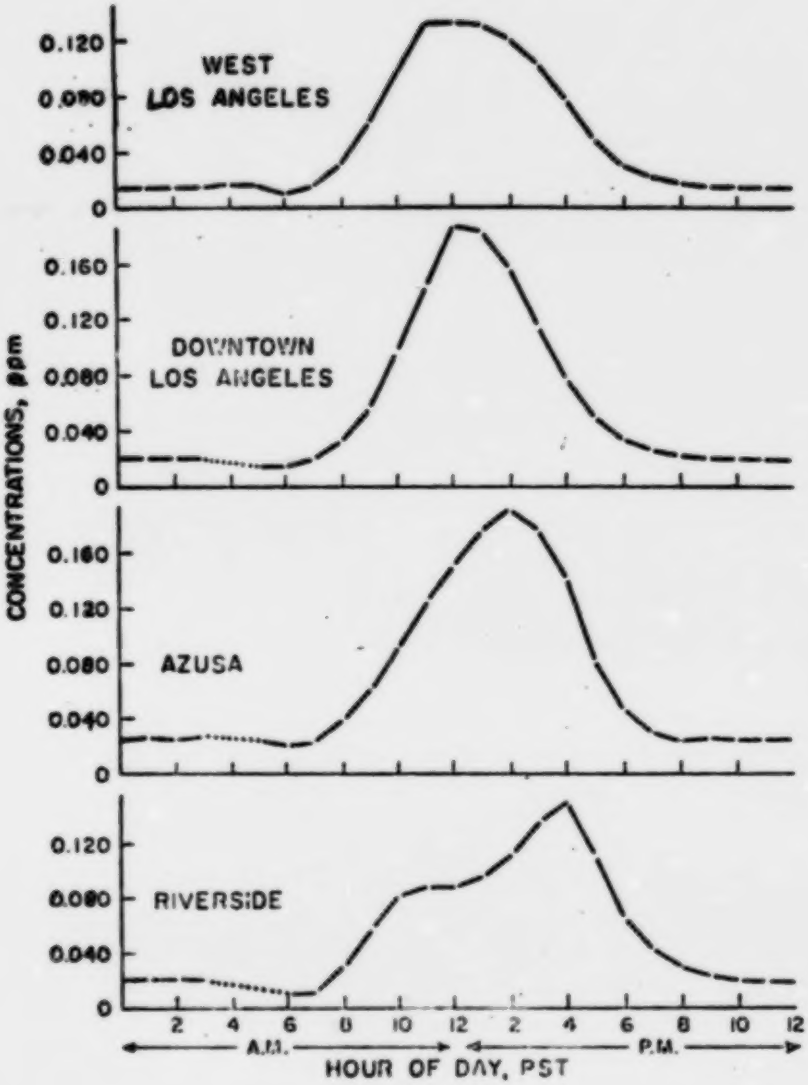


Figure 5-7. OXIDANT MONTHLY MEAN HOURLY AVERAGE CONCENTRATIONS--OCTOBER 1965.

The station at West Los Angeles is about 10 miles west, Azusa about 20 miles east, and Riverside about 60 miles southeast of the central Los Angeles station. As shown, the time of peak oxidant concentration progressively becomes later from west to east. This coincides with the daytime ocean-to-land movement of air regularly observed in California coastal regions from spring to fall months. There is indication of another but earlier peak in Riverside which is generally attributed to local pollution sources.

The supposition that the rather high oxidant concentrations in less densely populated Azusa and Riverside are at least in part due to pollution transport is given strength by the carbon monoxide traces for the same areas as shown in Figure 5-8. The times of peak CO values are much the same for all four locations, but the concentrations are lower in Azusa and Riverside as compared to West and central Los Angeles. The conclusion reached by confirming inspection of these figures with information gained from Chamber studies is that under the conditions present, the rate of oxidant formation in the air mass moving from west to east over the Los Angeles basin and inland valleys exceeded the dilution effect.

In almost all metropolitan areas of the United States outside of California, oxidant data are presently available from only one,--or at most a few--locations. However, particular combinations of source strength variations in hydrocarbons and nitrogen oxides and in patterns of air mass transport may contribute to the same type of contaminant concentration and time variation as just shown for the Los Angeles area. Thus we should not be surprised at any deviations from present patterns as information from augmented air monitoring networks becomes available.

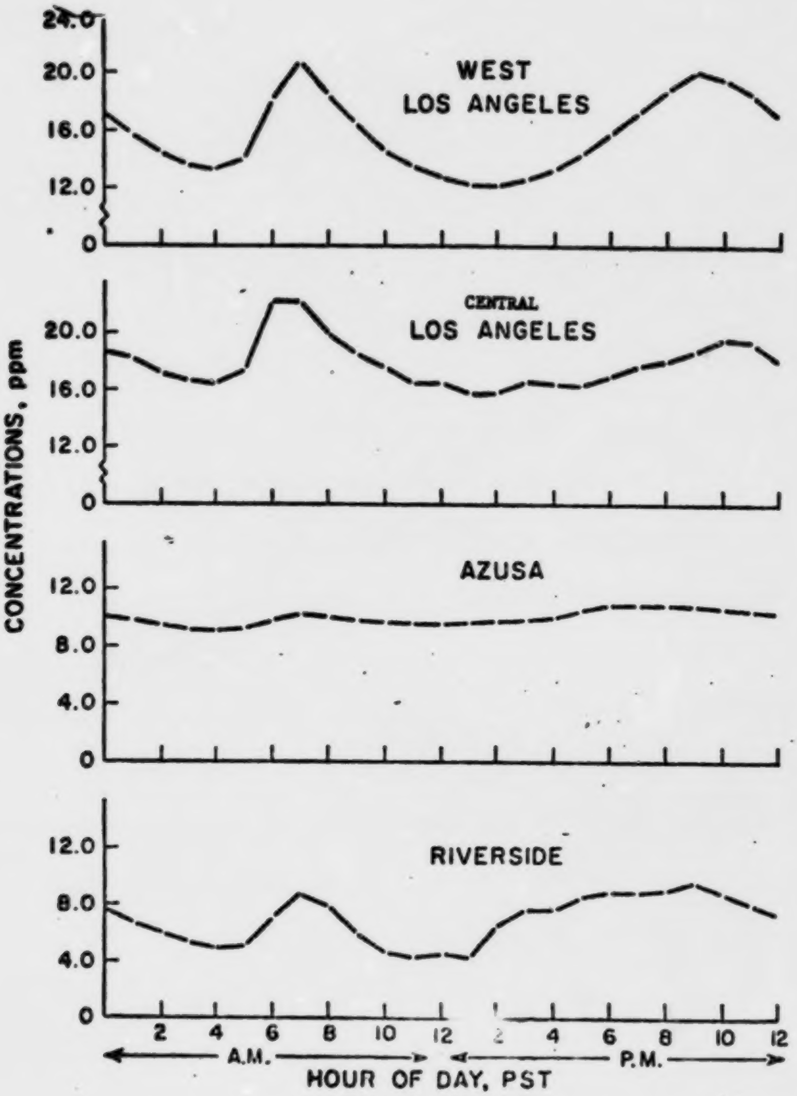


Figure 5-8. CARBON MONOXIDE MONTHLY MEAN HOURLY AVERAGE CONCENTRATIONS--OCTOBER 1965.

b. Seasonal Variations

The seasonal variation by month for the major contaminants involved in or resulting from atmospheric photochemical reactions depends upon whether the contaminant is consumed or produced on a net basis during daylight hours. For nitric oxide and hydrocarbons, as with most primary contaminants, higher mean values are observed during late fall and winter months. There is less overall atmospheric mixing during these months in most cases and less consumption to form products.

Total oxidant, as indicated previously, typically exhibits a seasonal peak during the period from early summer to early fall. This is, of course, the time of year when more intense short wavelength solar irradiation reaches the earth's surface. On the west coast of the United States a persistent late summer and early fall subsidence temperature inversion and less cloud cover enhance the potential for high oxidant levels.

The pattern for nitrogen dioxide is not quite so distinct. The more efficient photochemical oxidation of nitric oxide in the summer is somewhat offset by the slower nitrogen dioxide disappearance rate in the winter. Thus varied and somewhat differing patterns are observed from city to city.

Figure 5-9 shows the seasonal variations by month in average total oxidant concentrations for the cities of Los Angeles, Denver, Phoenix and Bayonne. The month-by-month variation in the maximum hourly mean is shown for the same cities in Figure 5-10. In all locations the overall mean and maximum hourly mean concentrations are higher during the summer months, although the peak period for Los Angeles is somewhat later. A number of factors includ-

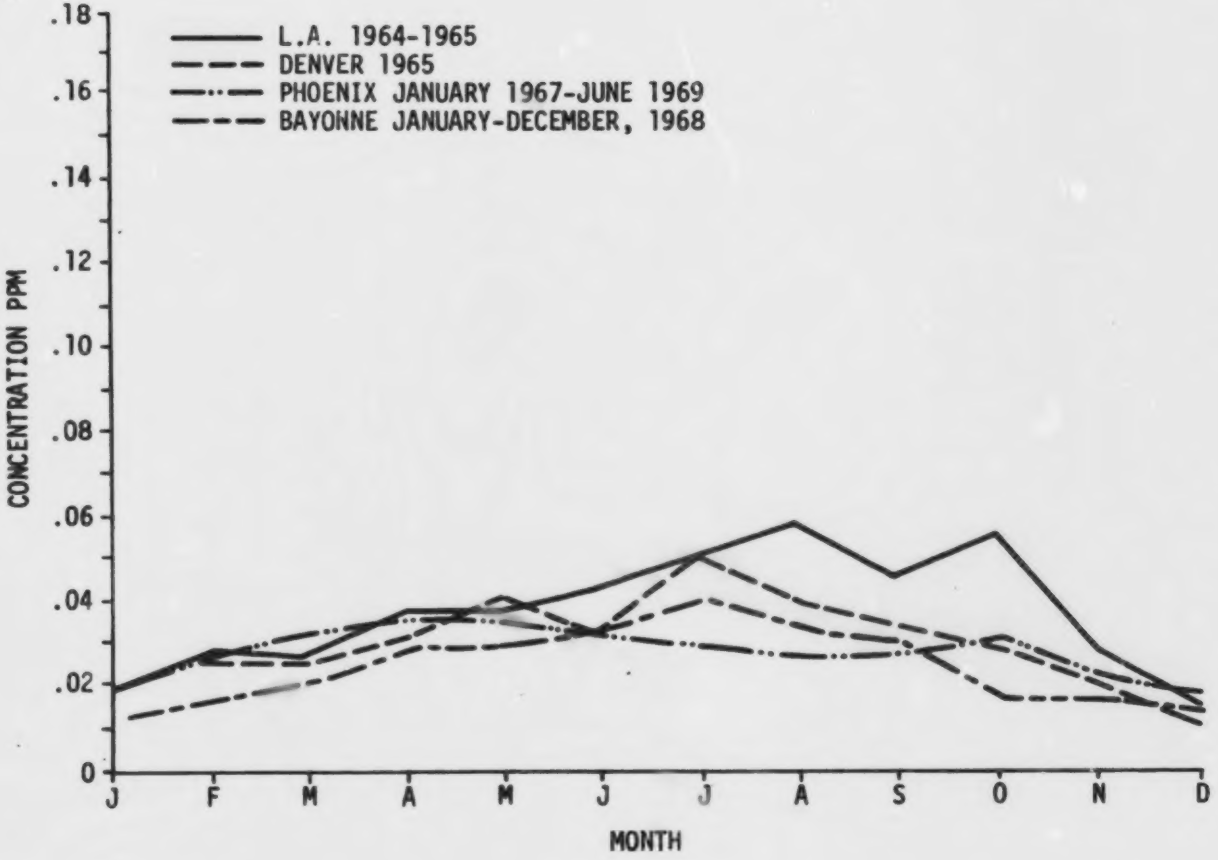


FIGURE 5-9. OXIDANT CONCENTRATION BY MONTH (MEAN OF ALL HOURS).

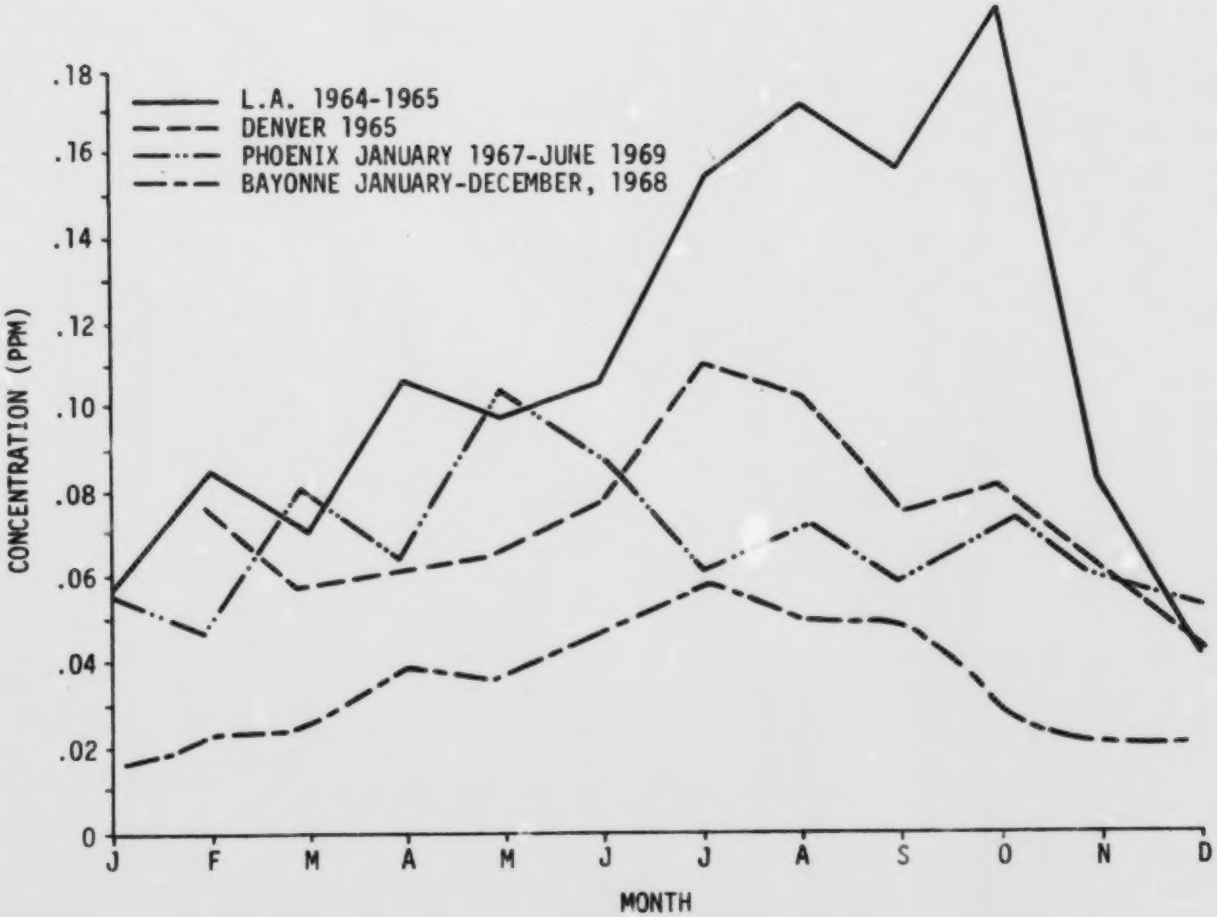


FIGURE 5-10. OXIDANT CONCENTRATION BY MONTH (MEAN OF MAXIMUM HOURS).

ing less cloud cover, lower wind speeds and stronger inversions account in part for this difference.

Figure 5-11 shows the seasonal patterns in nitric oxide by presenting the mean values by month of year during the time period indicated for the cities of Chicago, Denver, Bayonne, and Los Angeles. The distinctly higher winter time levels are evident.

The seasonal variation in nitrogen dioxide shown by monthly mean values for the same cities is shown in Figure 5-12. Here the pattern is less distinct and varies from location to location.

3. Ozone vs. Oxidant Measurements

Almost from the beginning of concern about photochemical air pollution, questions have been raised about the true ozone concentrations in the atmosphere, and the extent to which this compound comprises so-called total oxidant values. Numbers of methods have been proposed which either theoretically or empirically are claimed to give results specified for ozone. These are treated more fully in paragraph D. of this chapter.

The principal problems associated with measurement of ozone with an oxidation-reduction reaction such as that used in the potassium iodide total oxidant method are positive interference from nitrogen dioxide and negative interference from sulfur dioxide. In the case of nitrogen dioxide, the positive interference is variable depending upon specific instrument configuration and potassium iodide concentration used.[13, 14, 15, 16] For the colorimetric type analyzers used in the CAMP network, and many state and local systems, a reasonable estimate is that nitrogen dioxide gives a response equal to

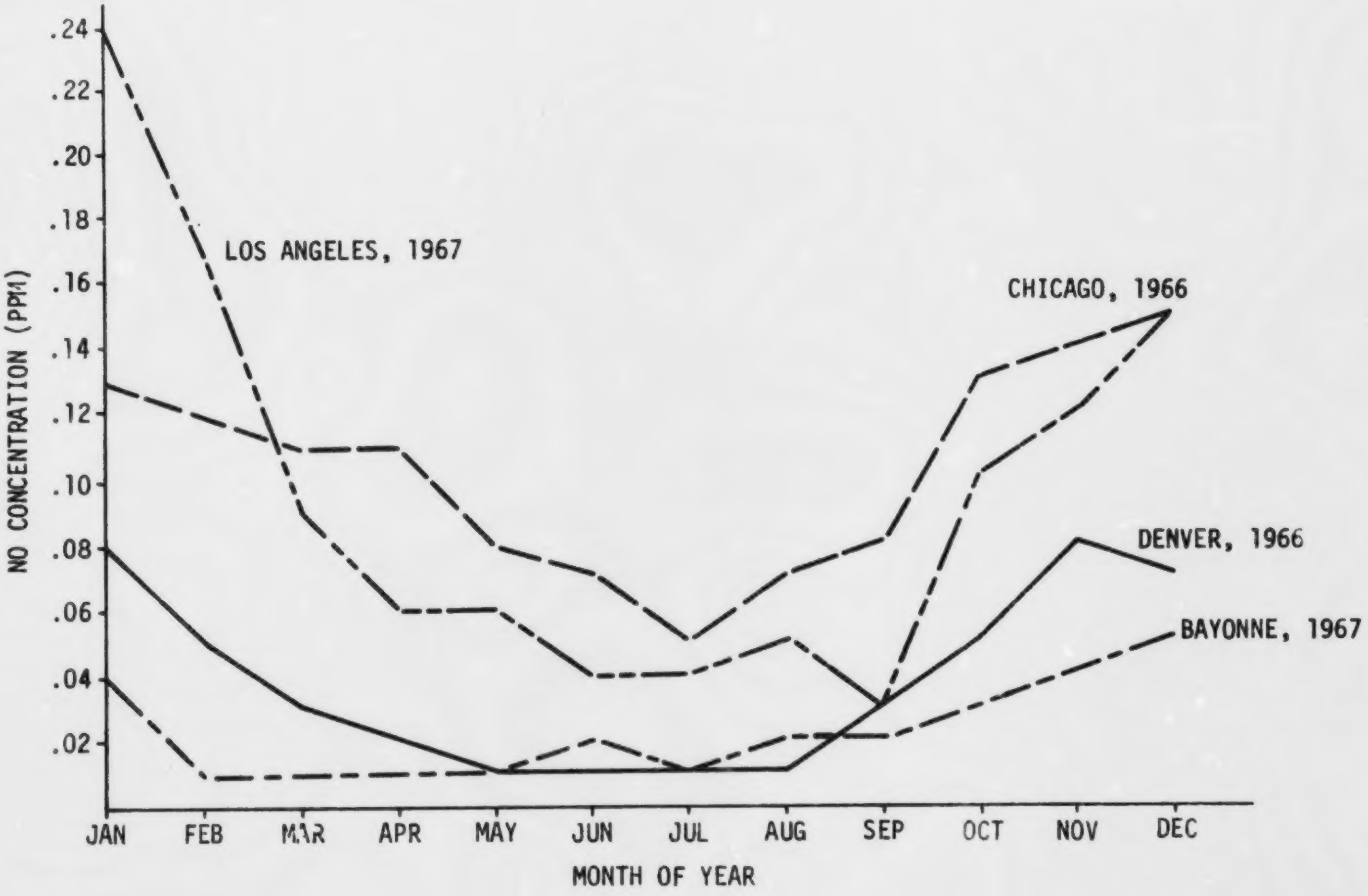


FIGURE 5-11. MEAN MONTHLY NO CONCENTRATIONS.

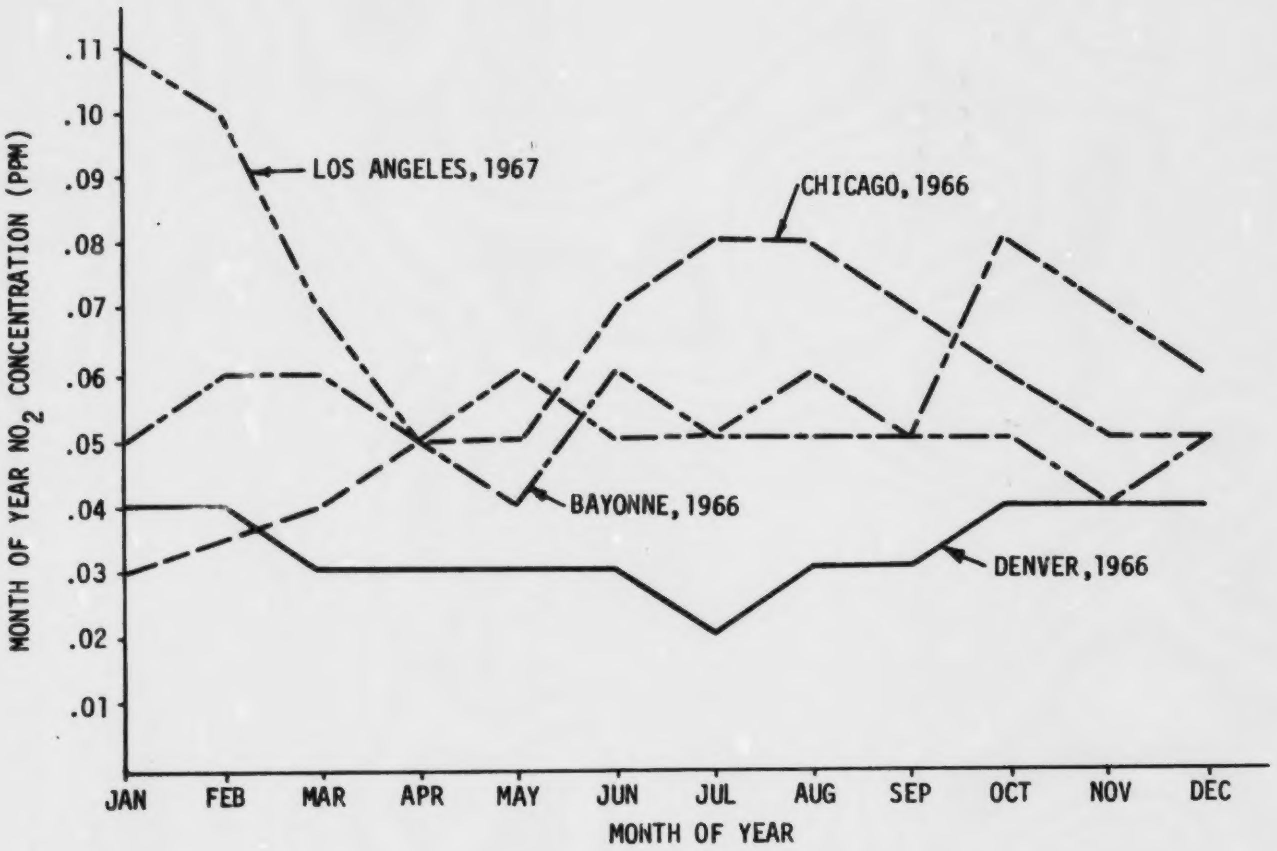


FIGURE 5-12. MEAN MONTHLY NO_2 CONCENTRATIONS.

20 percent of its concentration.

Other positive interferences are possible (such as from PAN), but under normal circumstances are of minor concern. It is true, however, that in some locations oxidant concentrations found are higher than would be expected for the time of day or year. An example is the St. Louis CAMP station, which is located near a large chemical complex. Occasional high oxidant concentrations, including one at 0.85 ppm, do not coincide with the usual diurnal end seasonal pattern. The National Air Pollution Control Administration has found it necessary to exclude high levels occurring before 11:00 A.M. and after 4:55 P.M. in listing maximum concentrations for its CAMP stations.

A potentially more serious interference in the measurement of ozone by the potassium iodide method is the negative response caused by sulfur dioxide. It acts in the reagent by reducing the iodine to the colorless iodide form. The negative response is equal to the sulfur dioxide concentration, up to the limit of the total oxidant originally present. As an example, the response of an oxidant analyzer to a stream containing 0.5 ppm ozone and 0.5 ppm sulfur dioxide would be zero. The response to a strema containing 0.25 ppm ozone and 0.5 ppm sulfur dioxide would also be zero. This is important to remember when considering some of the adjusted oxidant data presented in the next few pages.

Of all the approaches to obtaining true ozone concentrations only a few have been used extensively enough to provide much data. These would include the ultraviolet photometric[15] and the chemiluminescent[98] methods.

An approach to eliminating the sulfur dioxide but not nitrogen dioxide interference is the use of chromium trioxide scrubbers which remove sulfur dioxide. These were incorporated in all CAMP stations except San Francisco at the beginning of 1964.[9] They are not used in the Los Angeles County network. One slight disadvantage particularly in areas with little sulfur dioxide results from the conversion by the scrubbers of nitric oxide to nitrogen dioxide, thus increasing the positive interference.

Efforts have also been made to correct the total oxidant concentrations by adjustment of the data to remove the effects of nitrogen dioxide and sulfur dioxide. This assumes that such data are available. It also is done on a fixed and arbitrary basis, and thus may not represent reality. The concentrations of oxidant for a summer and a winter month for each of four stations are adjusted for nitrogen dioxide in Tables 5-2 and 5-3.

Table 5-2 lists the monthly mean concentrations, while Table 5-3 lists the monthly means at daily maximum hourly average concentrations. The adjustment was performed by subtracting a sum equal to one-fifth of the nitrogen concentration for the same period from each total oxidant concentration. As mentioned earlier the nitrogen dioxide interference is known to be variable, particularly from analyzer to analyzer, so the correction cannot be assumed to be perfect in any sense. There is a further complication in that the nitrogen dioxide analyzer tends to "smooth" the true concentrations more than does the oxidant analyzer because it responds more slowly. Since hourly averages are calculated over fixed time periods, there is more likelihood that a nitrogen dioxide concentration occurring in the atmosphere at a

Table 5-2. OXIDANT CONCENTRATIONS ADJUSTED FOR NITROGEN DIOXIDE RESPONSE MONTHLY MEANS OF HOURLY AVERAGE CONCENTRATIONS, ppm

	Station	Month	Concentration, ppm Unadjusted	Concentration, ppm Adjusted	Percent Due to NO_2
Summer Months	Los Angeles	July 1964	0.055	0.044	20
	Sacramento	July 1965	0.042	0.036	14
	Denver	July 1965	0.048	0.041	15
	St. Louis	July 1964	0.035	0.029	17
Winter Months	Los Angeles	Jan 1965	0.021	0.005	76
	Sacramento	Jan 1965	0.020	0.015	25
	Denver	Feb 1965*	0.029	0.019	35
	St. Louis	Jan 1965	0.024	0.020	17

* 12 days of data only

Table 5-3. **OXIDANT CONCENTRATION ADJUSTED FOR NITROGEN DIOXIDE RESPONSE MONTHLY MEANS OF DAILY MAXIMUM HOURLY AVERAGE CONCENTRATIONS**

	Station	Month	Concentration, ppm Unadjusted	 Adjusted	Percent Due to NO_2
	Los Angeles	July 1964	0.166	0.154	7
Summer	Sacramento	July 1965	0.085	0.075	12
Months	Denver	July 1965	0.110	0.098	11
	St. Louis	July 1964	0.078	0.071	9
	Los Angeles**	Jan 1965	0.037	0.020	46
Winter	Sacramento	Jan 1965	0.035	0.028	20
Months	Denver	Feb 1965*	0.073	0.060	18
	St. Louis	Jan 1965	0.046	0.040	13

* 12 days of data only

** 9 days of data when NO_2 measured at time of maximum hourly average oxidant concentration particular time period will be partially reflected at a later instrument time than will the reading on the oxidant analyzer. This effect would tend to disappear when averaging results over a month as in Tables 5-2 and 5-3, but could be of consequence in individual values.

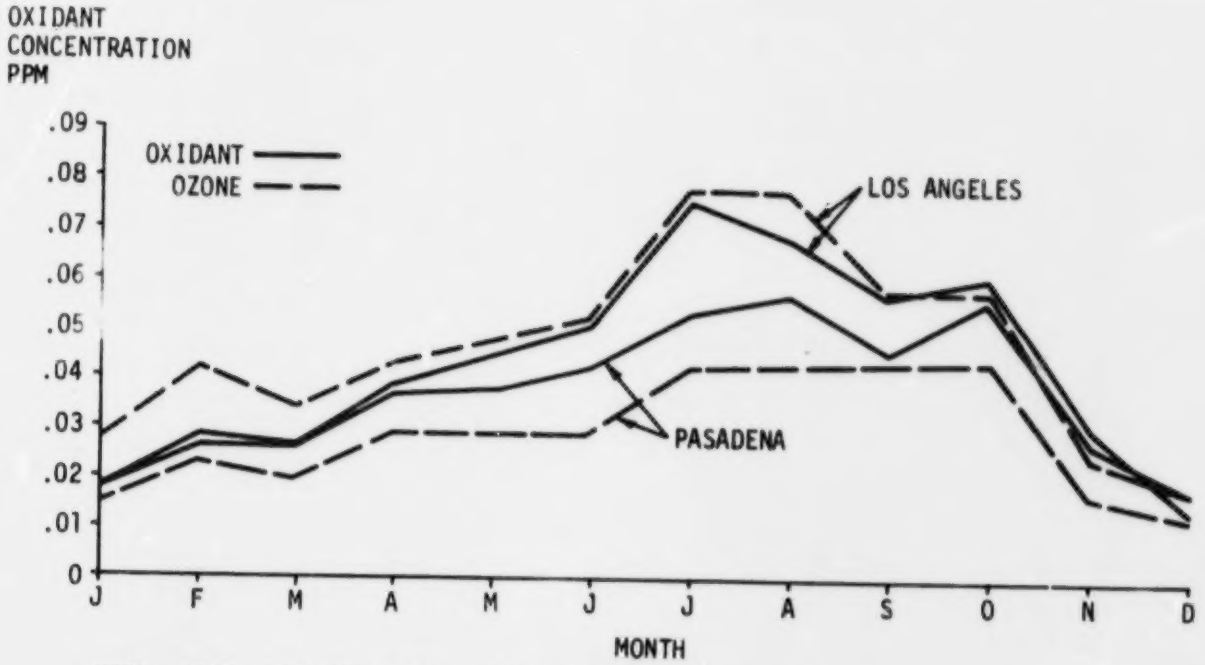
Nevertheless, the tables show that the adjustment is generally greater during the specified winter months than during the specified summer months. They further show that adjustment is less for maximum hourly averages than for overall averages. It is also interesting to note that greatest change in percent effect from winter to summer is for Los Angeles. The absolute adjustment in all cases varies little from .01 ppm.

For several years the Los Angeles County Air Pollution Control District operated ultraviolet photometers as an approach to specific ozone measurement. In most cases they were operated in parallel with potassium iodide total oxidant analyzers. Although there were substantial operational and maintenance problems, a substantial quantity of what is believed to be valid data were produced.

In Figure 5-13, the monthly means of the hourly average concentrations of ozone are compared to concentrations of oxidants in Pasadena and in Los Angeles. In Figure 5-14, the monthly means of the maximum hourly averages are compared. In Figure 5-15 hour-by-hour values for ozone and oxidant concentrations for Los Angeles and Pasadena are shown for the month of July, 1964.

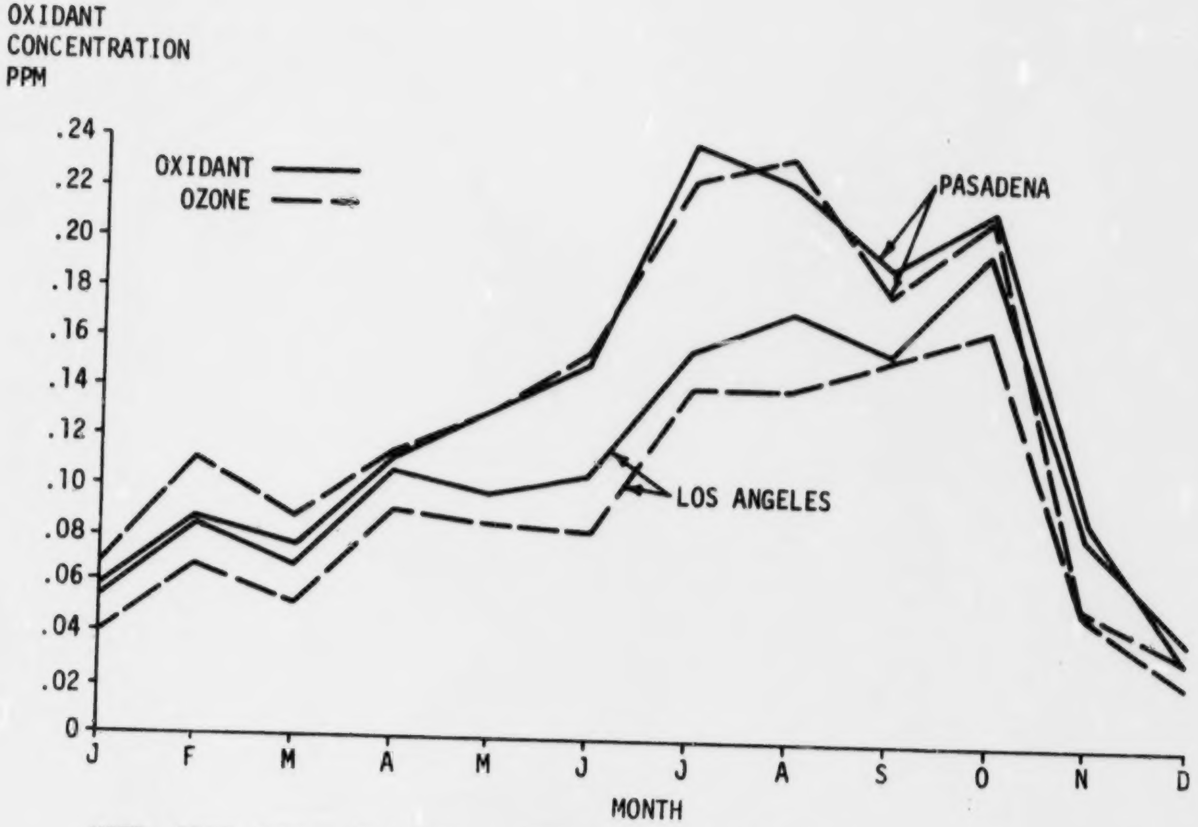
The term "adjusted" oxidant in the three foregoing figures is calculated from the following expression

$$\text{Adjusted oxidant} = \text{OX}-1/5\text{NO}_2+\text{SO}_2$$



NOTE: SEPT.,OCT.,NOV.,DEC., OZONE DATA FOR 1964 ONLY.

FIGURE 5-13. COMPARISON OF OZONE AND OXIDANT MONTHLY MEAN OF HOURLY AVERAGE CONCENTRATIONS--LOS ANGELES AND PASADENA, 1964-1965.



NOTE: SEPT, OCT., NOV., DEC., OZONE DATA FOR 1964 ONLY.

FIGURE 5-14. COMPARISON OF OZONE AND OXIDANT MONTHLY MEAN OF MAXIMUM HOURLY CONCENTRATIONS--LOS ANGELES AND PASADENA, 1964-1965.

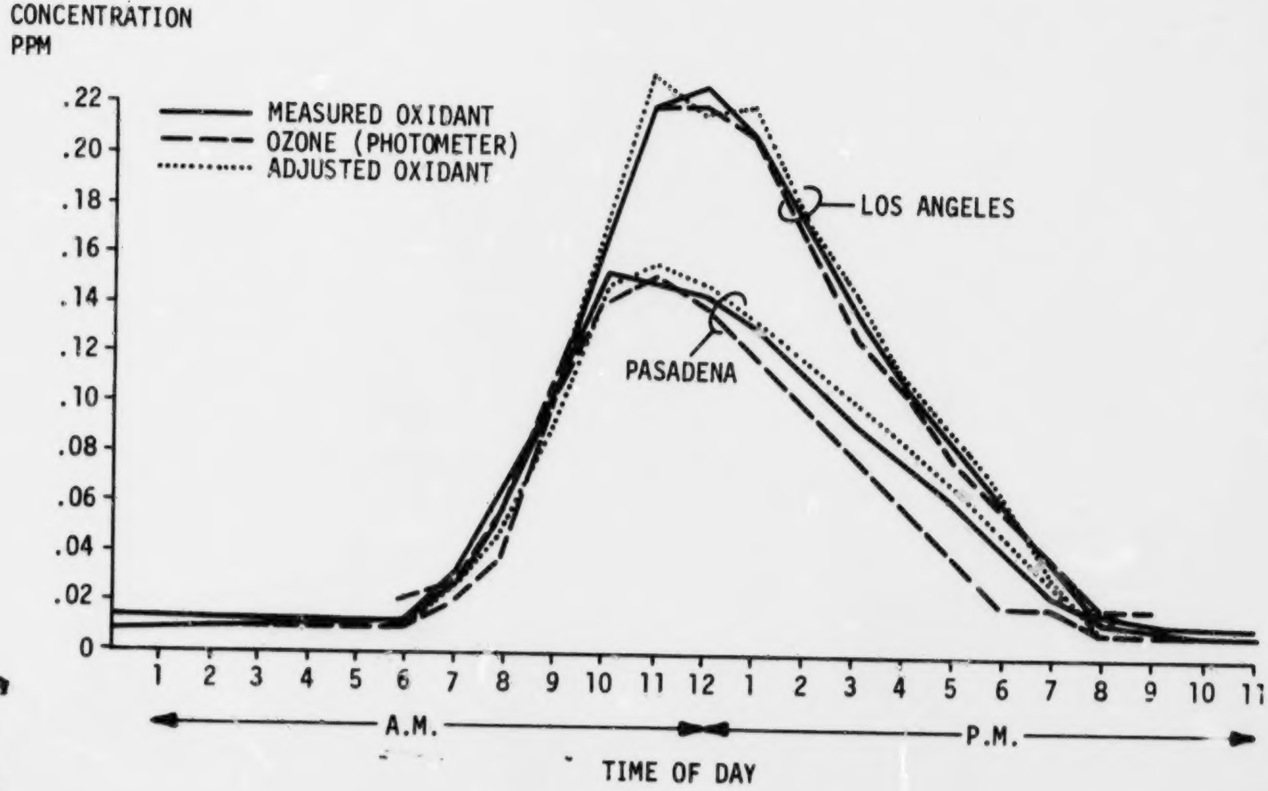


FIGURE 5-15. COMPARISON OF OZONE, OXIDANT AND OXIDANT ADJUSTED FOR NO_2 AND SO_2 RESPONSE--LOS ANGELES AND PASADENA, JULY 1964.

These quantities are, respectively, the measured oxidant, nitrogen dioxide and sulfur dioxide concentrations. There is a possibility of an overcorrection for sulfur dioxide if it exceeds the real ozone concentration. However, this is very unlikely in daylight hours for the locations used because of the routinely low sulfur dioxide concentrations experienced.

The close agreement between adjusted oxidant and ozone concentrations indicated that the contribution to the oxidant measurement by PAN or other oxidants is very low at the locations involved. This is as expected as far as photochemical sources of these other oxidants is concerned. Agreement between the unadjusted oxidant and ozone is also good, but this may be partly becuase interferences by NO_2 and SO_2 compensated for one another.

In a recent study made by the Research Triangle Institute under contract with the U.S. Public Health Service, the chemiluminescent method for ozone was used in several cities.[99,100] The mean hourly ozone concentrations for each of these cities during the period of sampling are shown in Figure 5-16. The diurnal patterns on selected days for the Denver and Philadelphia CAMP sites are shown in Figure 5-17. The physical appearance of these curves tends to indicate a high degree of similarity to typical total oxidant traces.

The data so far available would seem to indicate that, by using caution, total oxidant data can be used to judge air quality effects related both to those based upon ozone and oxidant, there are situations where negative interference from sulfur dioxide and positive interference from other oxidants could cause difficulties in data interpretation. For this reason it would be desirable to continue both laboratroy and field studies on more specific methods for ozone.

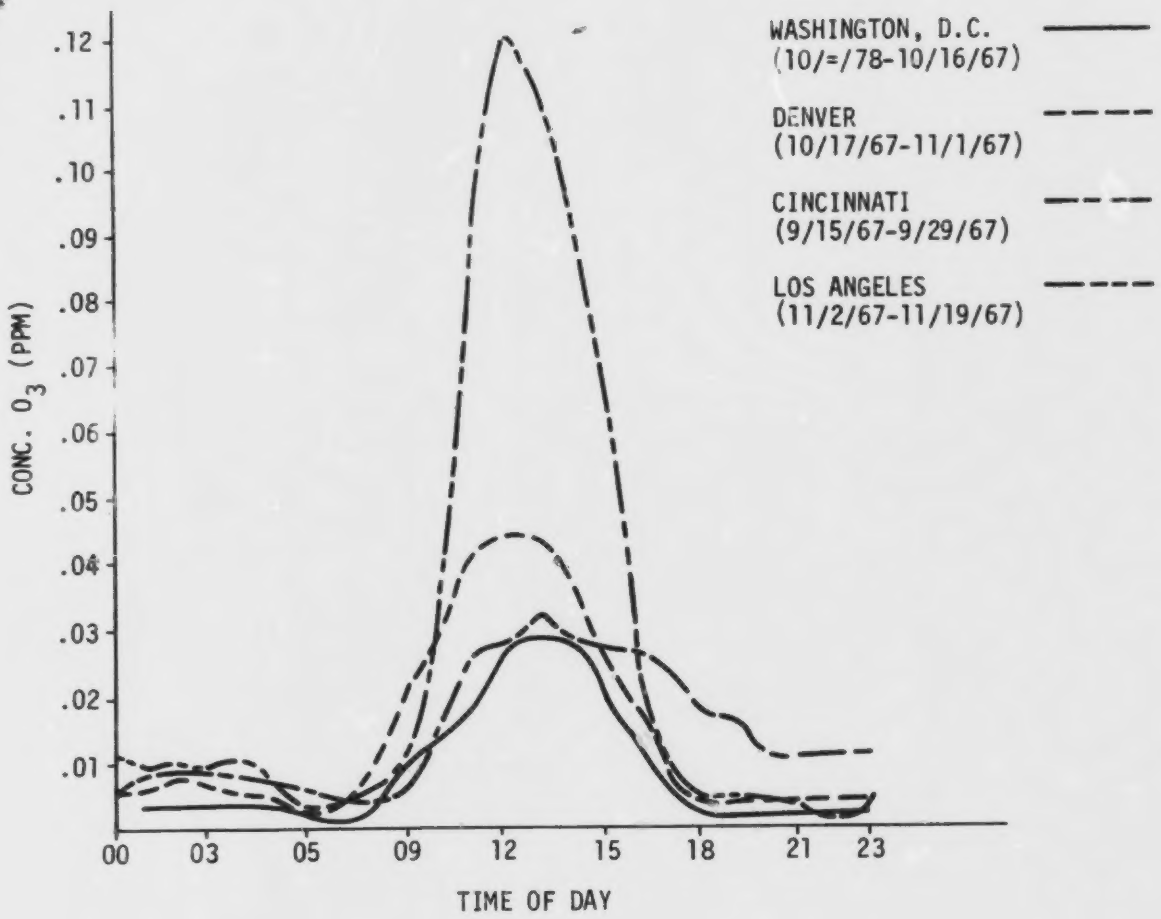


FIGURE 5-16. AVERAGE OZONE CONCENTRATIONS BY HOUR.

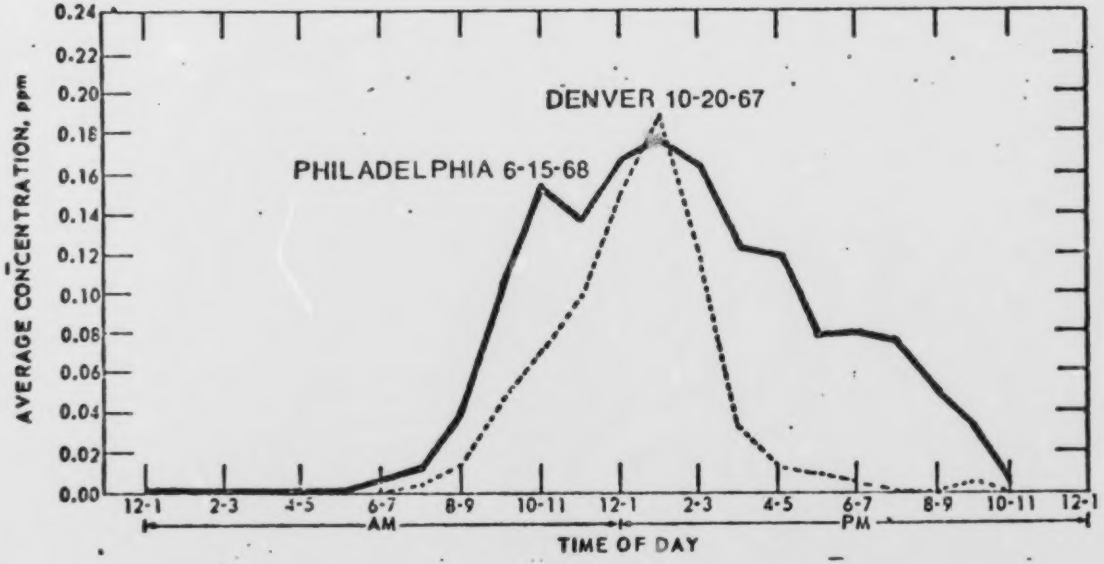


Figure 5-17. DIURNAL VARIATION OF OZONE CONCENTRATION IN PHILADELPHIA AND DENVER.

4. Observed Contaminant Concentrations

a. Oxidant

Information in the previous subparagraphs has shown that the shape of the diurnal and seasonal oxidant concentrations are generally similar over a broad geographic spectrum of locations. However, on the basis of presently available data, the frequency of occurrence and the severity of ozone and other oxidant episodes varies considerably among even the larger metropolitan areas.

Table 5-4 gives the cumulative distribution of hourly mean oxidant levels for the six CAMP cities and five locations in California for the period 1964-1965. One fact immediately apparent is that the yearly average concentrations vary over a much smaller range than does the value which is exceeded 1 percent of the time at each location. In fact, the range over which the yearly averages vary is little different from that observed in remote, sparsely populated areas (see Chapter 2). A prime reason for this apparent anomaly is that the yearly averages are unduly weighted by nighttime values. In locations having substantial photochemical air pollutions problems, ozone-scavenging compounds (principally NO) are injected into the atmosphere with the late afternoon traffic with the result that nighttime ozone values are often very low.

Table 5-5 shows, for the same locations as in Table 5-4, the number of days with maximum hourly oxidant averages exceeding the levels 0.15, 0.10 and 0.05 ppm. The number of days with at least one hourly average above 0.15 ppm oxidant is an order of magnitude greater for Pasadena and Los Angeles as

Table 5-4. CUMULATIVE HOURLY AVERAGE OXIDANT CONCENTRATIONS (1964-1965).

City	Percent of Hours with Concentrations Equal to or Greater than Stated Concentrations, ppm								Yearly Average (1964-1965)
	90	70	50	30	10	5	2	1	
Pasadena	.01	.01	.02	.04	.12	.18	.23	.26	0.042
Los Angeles	.01	.01	.02	.04	.10	.14	.18	.22	.036
San Diego	.01	.02	.03	.04	.08	.10	.12	.14	.036
Denver*	.01	.02	.03	.04	.06	.08	.10	.12	.036
St. Louis	.01	.02	.03	.04	.06	.07	.09	.11	.031
Philadelphia	.01	.02	.02	.03	.06	.08	.11	.14	.026
Sacramento	.01	.01	.02	.04	.06	.08	.10	.12	.030
Cincinnati	.01	.02	.02	.04	.06	.07	.08	.10	.030
Santa Barbara	.02	.02	.03	.04	.06	.08	.09	.10	.036
Washington, D.C.	.01	.01	.02	.03	.06	.07	.09	.10	.029
San Francisco	.01	.01	.02	.03	.04	.05	.06	.07	.019
Chicago	.01	.01	.02	.03	.05	.06	.08	.08	.028

* Eleven months of data beginning February, 1965

Source: See Reference 38 and 39

Table 5-5. OXIDANT CONCENTRATIONS (1964-1965).

Station	Days with Maximum Hourly Average Equal to or Greater Than Concentration Specified						Maximum Hour Average	Peak Concentrations
	0.15 ppm		0.10 ppm		0.05 ppm		(ppm)	(ppm)
	Days	Percent	Days	Percent	Days	Percent		
Pasadena	299	41.1	401	55.1	546	75.0	0.46	0.67
Los Angeles	220	30.1	354	48.5	540	74.0	0.58	0.65
San Diego	35	5.6	130	20.9	440	70.6	0.38	0.56
Denver*	14	4.9	51	17.9	226	79.3	0.25	0.31
St. Louis	14	2.4	59	10.1	362	62.2	0.35	0.85
Philadelphia	13	2.3	60	10.9	233	41.9	0.21	0.25
Sacramento	16	2.3	104	14.6	443	62.3	0.26	0.45
Cincinnati	10	1.6	55	9.0	319	52.0	0.26	0.32
Santa Barbara	11	1.5	76	10.5	510	70.5	0.25	0.28
Washington, D.C.	7	1.2	65	11.3	313	54.2	0.21	0.24
San Francisco	6	.9	29	4.5	185	28.6	0.18	0.22
Chicago	0	0	24	4.5	269	50.8	0.13	0.19

* Eleven months of data beginning February, 1965

compared to the other ten cities. The unusually high peak value of 0.85 ppm for St. Louis has been referred to earlier. This station is located near a large chemical complex, with the distinct possibility that this high concentration --as well as others--may be due to interferring emissions from some unidentified source.

Other oxidant information is presented for the same twelve cities in Table 5-6. The month having the highest mean oxidant concentration, the overall mean for the month, and the mean of the maximum hourly concentrations are shown.

Data for the CAMP locations for the years 1966-1967 plus several locations reporting to the USPHS New York-New Jersey Abatement Project for 1967 or 1968 are shown in Table 5-7. This information is in the same form as Table 5-4, showing number of days with at least one hourly average equal to or exceeding the state levels. While some year-to-year variation is indicated for the CAMP stations, it is not ususual. The three locations in the New York Metropolitan Area show oxidant levels that fit within the range of the CAMP cities.

Data for a number of contaminants were recently assembled by the California Air Resources Board prior to Hearings on State Air Quality Standards.[101] This included a report by month and year for 1967 on the number of days the maximum hourly oxidant concentration at each of 39 stations exceeded 0.10 ppm. Every station in the state except Berkeley, Richmond, and San Francisco exhibited maximum hourly averages above this level for at least 5 percent of the days. In many locations in Los Angeles County this level is exceeded on more than 50 percent of the days. One or more stations in Orange, Riverside,

Table 5-6. HIGHEST MONTHLY MEAN OXIDANT CONCENTRATIONS (1964-1965).

Station	Highest Month (all hours)	Mean of Hourly Average Concentrations (ppm)	Mean of Maximum Hourly Concentrations (ppm)
Pasadena	July	0.075	0.24
Los Angeles	August	0.056	0.17
San Diego	October	0.050	0.11
Denver*	July*	0.050	0.11
St. Louis	May	0.042	0.072
Philadelphia	July	0.054	0.11
Sacramento	June	0.040	0.075
Cincinnati	July	0.048	0.098
Santa Barbara		0.042**	0.064 and .072
Washington, D.C.	May	0.041	0.072
San Francisco	May	0.031	0.046
Chicago	April	0.044	0.070

* Eleven months of data beginning February, 1965

** 1964-1965 average for month of May the same as for September

Table 5-7. TOTAL OXIDANT CONCENTRATIONS EXCEEDING SELECTED LEVELS (1967-1968).

City	Year	Days of Valid Data	Number of Days 0.05 ppm	Maximum Hourly 0.10 ppm	Average Exceeding 0.15 ppm	Maximum Hourly Average
Chicago	1966	235	52	6	3	0.19
	1967	255	113	16	1	0.16
Cincinnati	1966	208	54	1	0	0.10
	1967	228	122	24	1	0.20
Denver	1966	298	187	46	9	0.19
	1967	166	76	12	4	0.21
Philadelphia	1966	315	145	52	19	0.52
	1967	282	124	28	3	0.15
St. Louis	1966	292	174	33	5	0.22
	1967	289	185	38	4	0.20
Washington, D.C.	1966	325	134	27	2	0.16
	1967	322	137	27	5	0.26
Staten Island*	1968	145	85	30	7	0.18
Bayonne	1968	365	120	15	2	0.18
Newark	1967	363	140	18	6	0.20

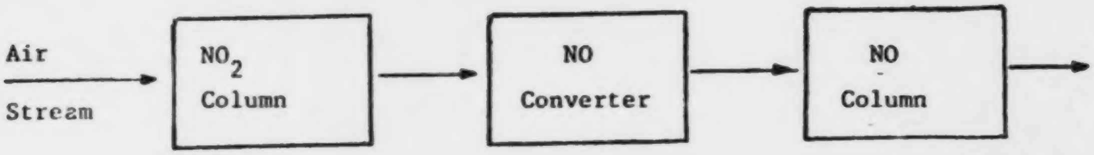
* August-December

San Bernardino, and San Diego Counties exceeded 0.1 ppm for more than 100 days during 1967.

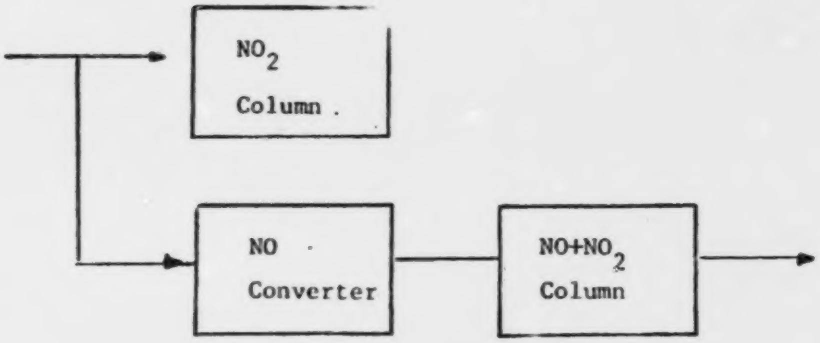
b. Nitrogen Oxides

Air quality data for these contaminants are limited to nitrogen dioxide (NO_2) and nitric oxide (NO). The method used, whether manually or instrumentally performed, is based upon the formation of a colored, organic reaction product of NO_2. Most data are from continuous analyzers which determine both NO_2 and NO on the same instrument, the NO being determined as NO_2 after passing through an oxidation unit. There are several flow schemes in use which may produce information not strictly comparable for NO.[102] These schemes are diagrammed below.

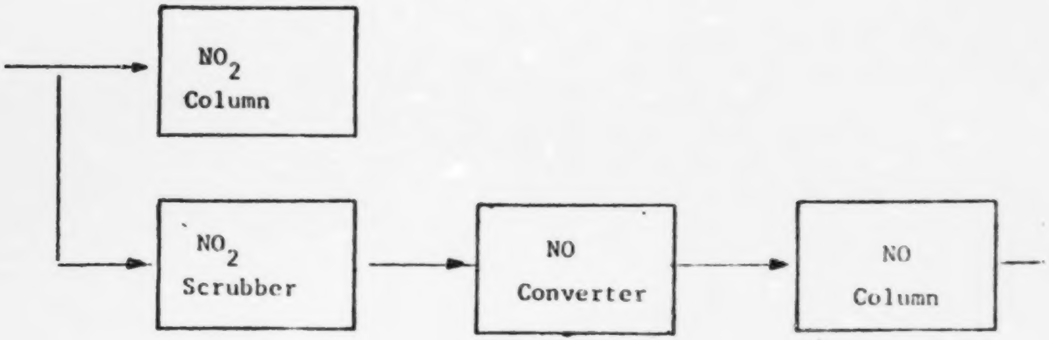
1) Series Flow:



2) Parallel (Mod. 1):



3) Parallel (Mod. 2):



Only the first two schemes are used to any extent, with the series approach predominating. In scheme 2) the NO must be determined by difference.

Of the two compounds, NO_2 is the most concern in regard to direct effects. However, by far the greatest portion of nitrogen oxides emissions is in the form of nitric oxide (see Chapter 2), which is therefore of prime importance in the photochemical reaction process. Data are presented below for both NO_2 and NO, and for their sum expressed as nitrogen oxides.

Table 5-8 shows nitric oxide and nitrogen dioxide data from the CAMP network in the form of cumulative frequency distributions of 5-minute values for the year 1966. The same type of information from selected cities in the State of California SCAN network is shown in Table 5-9, except that the concentrations represent 1-hour averages and the data are separated according to summer and winter. Please note that nitrogen-dioxide and nitrogen oxides (sum of NO and NO_2) are reported.

Data on nitrogen dioxide only were available from several stations

Table 5-8. CUMULATIVE FREQUENCY DISTRIBUTIONS OF 5-MINUTE VALUES--NITRIC OXIDE AND NITROGEN DIOXIDE (1966 CAMP).

City	Frequency Distribution--Percent of Values Equal to or Less Than Stated Concentration									
	.10	.30	.50	.70	.90	.95	.98	.99	Maximum	Arithmetic Mean
Cincinnati										
NO	.00	.01	.02	.04	.10	.16	.25	.33	1.18	.04
NO_2	.02	.03	.03	.04	.06	.07	.09	.10	.30	.04
Chicago										
NO	.02	.05	.09	.13	.20	.24	.31	.37	.74	.10
NO_2	.03	.04	.05	.06	.09	.11	.13	.15	.35	.06
Philadelphia										
NO	.01	.02	.03	.06	.13	.18	.29	.42	1.98	.06
[illegible]	.02	.03	.03	.04	.07	.08	.10	.11	.29	.04
Denver										
NO	.00	.01	.02	.04	.09	.14	.20	.26	.59	.04
NO_2	.02	.02	.03	.04	.05	.06	.09	.10	.35	.03
St. Louis										
NO	.00	.01	.02	.04	.08	.12	.17	.22	.61	.03
NO_2	.01	.02	.03	.04	.06	.07	.08	.09	.21	.03
Washington, D.C.										
NO	.00	.01	.02	.03	.08	.14	.25	.35	1.15	.04
NO_2	.02	.03	.03	.04	.06	.07	.08	.09	.19	.04

Table 5-9. CUMULATIVE FREQUENCY DISTRIBUTION OF HOURLY AVERAGE CONCENTRATIONS OF NITROGEN DIOXIDE AND NITROGEN OXIDES (1967 SCAN).

City	Frequency Percent							
	10	30	50	70	90	95	Maximum	Arithmetic Mean
Los Angeles								
NO_2 Summer		.03		.06	.09	.11	.43	.05
Winter	.02	.04	.06	.08	.15	.21	.54	.08
NO_x Summer			.08	.11	.20	.24	.86	.10
Winter	.05	.10	.16	.27	.49	.63	1.34	.22
Pasadena								
NO_2 Summer			.05	.06	.09	.11	.20	.06
Winter	.02		.05	.08	.14	.19	.37	.07
NO_x Summer		.05	.07	.10	.15	.17	.34	.09
Winter	.04		.11	.18	.32	.39	.71	.15
Sacramento								
NO_2 Summer		.02		.03	.04	.05	.15	.03
Winter	.01	.02	.03	.05	.07	.09	.30	.04
NO_x Summer		.02	.03	.04	.07	.09	.32	.04
Winter			.05	.10	.22	.32	1.14	.10
San Diego								
NO_2 Summer				.01	.02	.03	.34	.01
Winter			.02		.05	.07	.24	.02
NO_x Summer				.01	.04	.07	.34	.02
Winter	.00	.02	.04	.08	.22	.30	.84	.08
Riverside								
NO_2 Summer	.01	.02	.04	.06	.09	.10	.25	.05
Winter	.01	.02	.03	.04	.08	.12	.31	.04
NO_x Summer		.04	.06	.09	.13	.15	.31	.08
Winter	.02	.04	.08	.12	.21	.26	.67	.10
Oakland								
NO_2 Summer			.02	.03	.06	.08	.26	.03
Winter	.01	.02	.03	.05	.08	.11	.33	.05
NO_x Summer		.03	.04		.09	.12	.48	.05
Winter	.02	.04	.08	.14	.28	.35	1.06	.12

Table 5-10. CUMULATIVE FREQUENCY DISTRIBUTION OF HOURLY AVERAGE NITROGEN DIOXIDE CONCENTRATIONS (1967 NEW YORK-NEW JERSEY).

Location	Frequency Percent					
	50	90	95	99	Maximum	Arithmetic Mean
Staten Island						
July	.02	.04	.05	.09	.15	.03
December	.01	.04	.05	.08	.11	.02
Year ([illegible] months only)					.18	-
Bayonne						
July	.05	.09	.11	.14	.28	.05
December	.06	.08	.09	.14	.22	.05
Year					.28	.05
Newark						
July	.06	.10	.11	.15	.18	.07
December	.06	.08	.09	.12	.20	.06
Year					.36	.06

cooperating in the New York-New Jersey Abatement Study for the year 1967. Freqeuncy distribution data were available by the month. This information is shown in Table 5-10.

Examination of Tables 5-8 and 5-9 indicate that for many cities the long term (annual) mean nitrogen dioxide and nitric oxide concentrations are nearly equal. Nitric oxide, however, exhibits higher maxima and lower minima. This results from its injection into the atmosphere as a primary contaminant, often during times of reduced mixing capacity. During photochemical reaction it may nearly disappear. Nitrogen dioxide, on the other hand, is formed photochemically and is subject to simultaneous atmospheric mixing processes. Its rate of disappearance is slower than nitric oxide, but this too is subject to specific reaction and mixing conditions.

Peak values of nitric oxide above 1 ppm are experienced on a rather widespread basis. Nitrogen dioxide concentrations have rarely reached this level, with most of the known such occasions having occurred in the Los Angeles area. In most major urban areas, peak NO_2 concentrations are under 0.5 ppm.

Recalling Table 5-5, the two stations in the Los Angeles area had higher oxidant levels more frequently than the other cities listed. The same situation does not hold in the case of the nitrogen oxides. Although exact comparisons cannot be made in each case, examination of Tables 5-8, 5-9, and 5-10 shows that Chicago, Bayonne and Newark have nitrogen oxide patterns not unlike those of Los Angeles and Pasadena.

c. Hydrocarbons

In examining atmospheric hydrocarbon concentrations in relation to photochemical smog, several factors must be considered. First, as discussed in Chapter 2, there is an enormous variation in the tendency for different hydrocarbons to enter into the photochemical smog reaction sequence, some (like methane) being virtually inert. Second, the simpler and less laborious atmospheric hydrocarbon detection methods are likely to respond most strongly to methane and other alkanes. Third, methane is very often more abundant than all other hydrocarbons combined; there is, in fact, apparently a "geophysical" minimum worldwide level of methane of about 1.0-1.5 ppm.[103,104,105] This makes it important in assessing photochemical air pollution to be able to discriminate between methane and other more reactive hydrocarbons. Unfortunately this type of analysis is expensive and time-consuming, so that such data are not abundant. Nevertheless it is available, and in this subparagraph such observations are discussed.

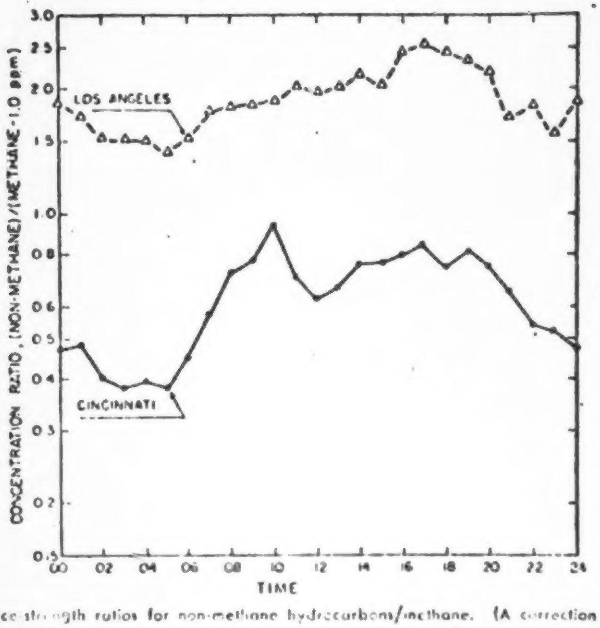
Although on occasion all other hydrocarbon concentrations drop to unmeasurably low levels, methane does not. There have been numerous measurements in remote, sparsely populated areas and far out on the ocean[105] which all suggest a worldwide minimum methane concentration of about 1.0 to 1.5 ppm. "Natural" sources of methane are mostly vegetation, especially in swampy areas. In inhabited areas methane levels are normally much higher; values of 6 ppm or more have been[106] observed. This is attributed to escape from petroleum and natural gas, although small amounts also result from combustion processes.

Ratios of nonmethane hydrocarbons (as carbon) to methane have been estimated for urban areas, after subtracting 1 ppm from methane values to allow for estimated biogenic background levels[106]. The nonmethane/methane hydrocarbon ratios for several weeks averaged 0.6 in Cincinnati and 1.9 in Los Angeles, although methane values were similar (Figure 5-18). The higher Los Angeles ratios evidently reflect the higher traffic densities.

In Table 5-11, hydrocarbons up to C_6 to C_7 as averaged in over 200 samples in the Los Angeles atmosphere (1) are tabulated on a molar basis. Note the great preponderance of methane. Even on a weight or carbon atom basis, methane would constitute about half the total hydrocarbon fraction; of the remainder, the saturated hydrocarbons (also relatively unreactive photochemically) also predominate. These samples were generally taken just before or during the morning traffic rush.

The proportion of aromatic to aliphatic[107] and some of the proportions among the aromatics have been studied[108]. Table 5-12 shows (again for Los Angeles) averages for aromatic concentrations observed in the atmosphere over several weeks sampling.

In Table 5-13 the diurnal patterns are given for the C_2 - C_5 hydrocarbons, showing the hour-by-hour variations averaged over some weeks in the Los Angeles smog season. All species listed reached a maximum in the morning, then declined through the midday (although there are irregularities in certain types)[99].



Source-strength ratios for non-methane hydrocarbons/methane. (A correction for the estimated background biosphere concentration of one ppm was deducted from the methane values.) Cincinnati, 574 hours during September 1954. Los Angeles, 213 hours during October to November 1964.

Figure 5-18. NONMETHANE/METHANE HYDROCARBONS RATIOS--CINCINNATI AND LOS ANGELES (1964)

Table 5-11. AVERAGE HYDROCARBON COMPOSITION--218 LOS ANGELES AMBIENT AIR SAMPLES (1965).

Compound	Concentration, ppm Molar		ppm in Methan
Methane		3.22	3.22
Ethane	.098		
Propane	.049		
Isobutane	.013		
n-Butane	.064		
Isopentane	.043		
n-Pentane	.035		
2,2-Dimethylbutane	.0012		
2-Methylpentane			
2,3-Dimathylbutane	.014		
Cyclopentane	.004		
3-Methylpentane	.008		
n-Hexane	.012		
Alkanes (beyond methane)		.3412	
Ethylene	.060		
Propene	.018		
1-Butane + Isobutylene	.007		
trans-2-Butane	.0014		
cis-2-Butane	.0012		
1-Pentene	.002		
2-Methyl-1-Butane	.002		
trans-2-Pentene	.003		
cis-2-Pentene	.0013		
2-Methyl-2-Butene	.004		
Propadiene	.0001		
1,3-Butadiene	.002		
Alkenes		.1020	
Acetylene	.039		
Methylacetylene	.0014		
Acetylene		.0404	
Benzene	.032		
Toluene	.053		
Aromatics		.0850	
TOTAL		3.7886	

Table 5-12. AVERAGE AND HIGHEST CONCENTRATION MEASURED FOR VARIOUS AROMATIC HYDROCARBONS.

Aromatic Hydrocarbon	Average Concentration ppm by Volume	Highest Measured Concentration, ppm by Volume
Benzene	0.015	0.057
Toluene	0.037	0.129
Ethylbenzene	0.006	0.022
p-Xylene	0.006	0.025
m-Xylene	0.016	0.061
o-Xylene	0.008	0.033
i-Propylbenzene	0.003	0.012
n-Propylbenzene	0.002	0.006
3- and 4-Ethyltoluene	0.008	0.027
1,3,5-Trimethylbenzene	0.003	0.011
1,2,4-Trimethylbenzene, *i*-Butyl- and Sec-Butylbenzene	0.009	0.030
tert-Butylbenzine	0.002	0.006
Total Aromatics	0.106	0.33

Table 5-13. AVERAGE ATMOSPHERIC LIGHT HYDROCARBON CONCENTRATIONS--DOWNTOWN LOS ANGELES--(FALL 1967).

Component, PPB Carbon*

Local Time	Days	Ethane	Ethylene	Acetylene	Propane	Propylene	Isobutane	n-Butane	Butylenes	Isopentane
0500	27	140	31	77	113	25	53	176	32	177
0600	28	140	49	112	113	36	61	200	34	224
0700	28	151	122	234	125	64	74	300	56	335
0800	31	145	102	212	126	54	75	304	49	346
0900	15	107	63	141	98	32	63	209	28	249
1000	33	126	67	152	118	38	64	260	34	303
1100	12	94	39	106	80	25	48	180	21	200
1200	32	106	39	101	108	20	63	200	15	199
1300	16	76	20	68	78	13	44	149	14	162
1400	38	94	26	74	97	17	57	156	19	155
1500	16	90	26	79	101	16	50	132	20	144
1600	34	75	39	95	81	24	46	139	21	141
East San Gabriel Valley (Azusa)										
0500	32	143	29	60	87	13	36	101	14	104
0600	33	128	17	65	76	15	31	98	12	103
0700	30	180	30	103	102	24	41	136	18	144
0800	32	118	37	101	84	20	44	149	18	160
0900	18	93	31	79	65	15	36	114	15	114
1000	32	86	24	69	66	19	40	132	15	136
1100	18	90	21	57	62	11	37	107	10	101
1200	30	89	15	50	58	10	40	98	9	93
1300	16	111	16	66	67	18	46	121	17	111
1400	42	97	18	64	75	17	50	121	18	117
1500	16	92	20	65	75	15	81	175	15	125
1600	37	79	21	58	76	14	41	122	14	123

* Parts per billion parts air, as carbon

Very few comparison studies have been conducted of hydrocarbon concentrations among various geographical locations. The study of Altshuller, Ortman, et al. compared methane and nonmethane hydrocarbons in Cincinnati and Los Angeles. Stephens and Burleson[110] have determined the hydrocarbon compositions for a number of air samples from widely scattered locations: Hawaii, Denver, New York, and Monterey-Salinas (California), as well as Riverside in Southern California. There are apparently substantial differences in proportions of individual hydrocarbons which may sometimes, but not always, be related to known differences in source contributions and extent of atmospheric reaction. However, there is much not yet fully explained in such data.

Laboratory work shows that in the photochemical reaction system there is a wide difference in the rate of disappearance or reaction of various hydrocarbons. These differences, for single hydrocarbons at least, may be related to structure: olefins and most aromatics are reactive, higher alkanes not very reactive, while benzene, acetylene and lower alkanes are virtually inert. In the atmosphere these differences have been harder to observe. Since the general effects of meteorological dilution plus continuing source emission obscure the effects of reaction,[109] Stephens and Burleson[111] studied the reaction of trapped atmospheric samples, artifically irradiated, and found that reactivities were much as expected from laboratory results. See Table 5-14.

The same authors[110] as well as others[109, 112] have also attempted to correlate observed atmospheric hydrocarbon concentrations with known emission sources. In general three sources--auto exhaust, natural gas, and

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Table 5-14. COMPARISON OF RESULTS FROM THE ULTRAVIOLET IRRADIATION OF AMBIENT AIR SAMPLES.

	Concentration in ppb					
	12/22/65			3/3/66		
Compounds	0 hour	24 hour	Percent Remain	0 hour	24 hour	Percent Remain
Ethane	38.5	38.4	99.5	37.6	35.2	93.7
Ethane	134.2	32.0	23.8	51.2	12.6	24.6
Propane	17.4	15.2	87.5	14.6	11.4	78.2
Propene	35.4	1.4	4.0	15.6	1.4	9.0
Propane	21.6	17.2	79.6	13.0	10.4	80.0
Propene	48.4	2.0	4.1	13.4	0.6	4.5
Isobutane	25.2	17.2	68.4	7.4	4.8	65.0
n-butane	119.0	78.5	66.0	44.8	27.2	60.7
Acetylene	310.5	262.0	84.6	69.6	56.8	81.6
1-butene	6.4	0.5	7.8	2.2	0.4	18.1
Isobutene	11.8	0.7	5.9	4.0	0.4	10.1
trans-2-butene	6.0	0.0	0.0	1.4	0.0	0.0
Isopentane	93.6	46.4	49.5	27.6	13.6	49.3
cis-2-butene	4.5	0.0	0.0	1.0	0.0	0.0
n-pentane*	60.0	30.0	50.0	18.6	5.8	31.2
1,3-butadiene	9.0	0.0	0.0	2.4	0.0	0.0
Methyl acetylene	9.5	5.0	52.6	2.0	1.2	60.0
2,2-dimethyl butane	2.3	1.7	74.0	0.6	0.4	66.6
1-pentene	5.0	0.0	0.0	1.0	0.0	0.0
2-methyl butene-1	8.9	0.0	0.0	2.0	0.0	0.0
trans-2-pentene	5.5	0.0	0.0	1.6	0.0	0.0
2,3-dimethyl butane	1.3	1.0	77.0	1.2	1.0	83.2
2-methyl pentane**	34.0	14.0	41.2	8.4	3.6	42.9
3-methyl pentane***	34.7	8.8	25.3	8.8	2.2	27.5
Cyclopentane	6.6	2.9	48.4	1.4	1.0	27.5
n-hexane	25.0	9.4	37.5	7.2	3.4	47.3
Cyclopentene	----	----	----	2.4	0.0	0.0

Note: First four compounds separated on chromatograph No. 2; remainder on chromatiograph No. 1.

* Contains 3-methyl butene-1

** Contains *cis*-2-pentene.

***Contains 2-methyl butene-2

gasoline vapor--, will account qualitatively for the observations. The quantitative agreement shows some discrepancies, however. (There is often an apparent excess of alkanes in the propane range over known source contributions.) These are not thought to be of great significance in atmospheric photochemistry, since these low-molecular weight alkanes are only very slightly reactive in the system, compared to unsaturated hydrocarbons.

Although details remain to be explained, the role of various hydrocarbons in atmospheric photochemistry is generally clear.

d. PAN

Utilizing gas chromatographic techniques with an electron capture detector, PAN concentrations were measured in Los Angeles during September and October 1965 by the California State Department of Public Health. Seven measurements per day were made for each of the 16 weekdays in September and 19 weekdays in October. The average concentrations by hour of day for these periods are shown in Figure 5-19. The measurements were made near the central Los Angeles air monitoring station, and the oxidant concentrations are shown for comparison with the PAN concentrations.

Beginning in June 1966, measurements of PAN have been made on the campus of the University of California at Riverside using the gas chromatograph and electron capture method described in paragraph G. of this chapter. Samples are usually collected once each hour between 7:00 A.M. and 4:00 P.M. PST. Other pollutants are also measured at the station operated by the Riverside Air Pollution Research Center and supported by the U.S. Public Health Service. In Figure 5-20, the average oxidant concentrations, measured with a Mast

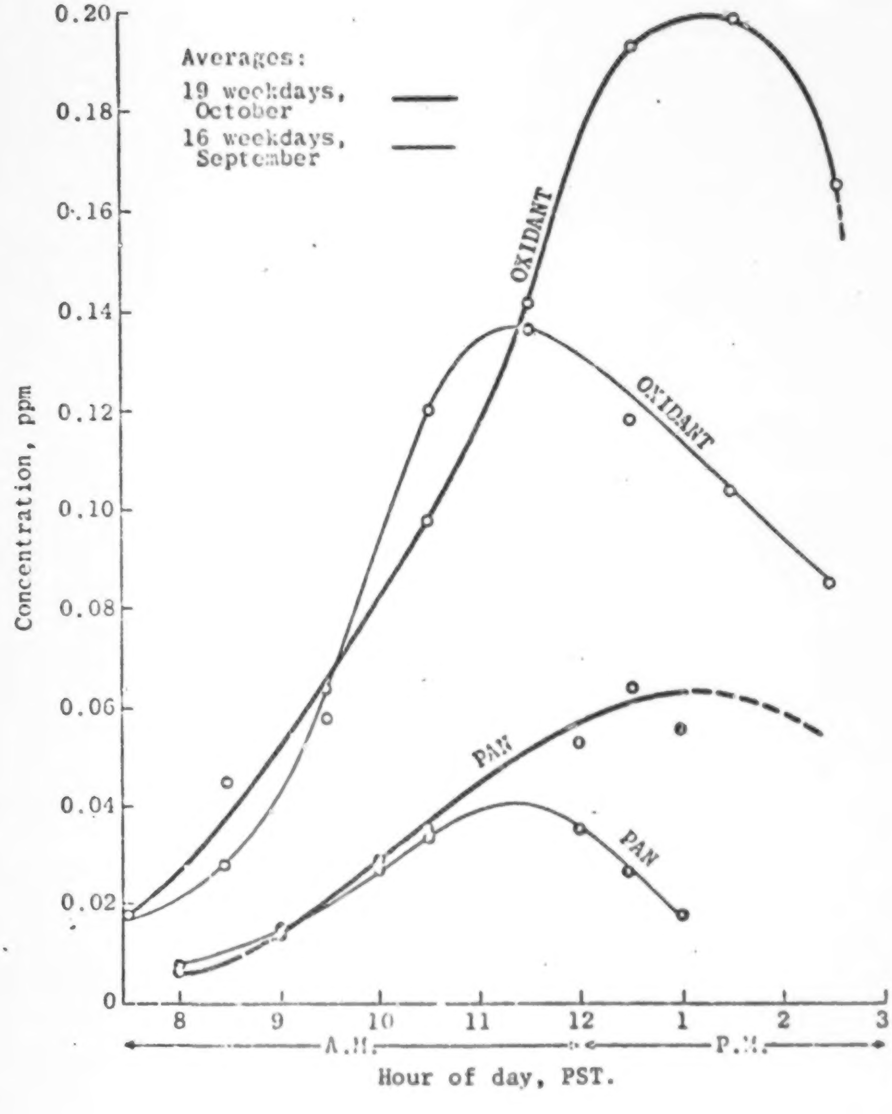


Figure 5-19. OXIDANT AND PAN CONCENTRATIONS BY HOUR OF DAY--DOWNTOWN LOS ANGELES--(1965).

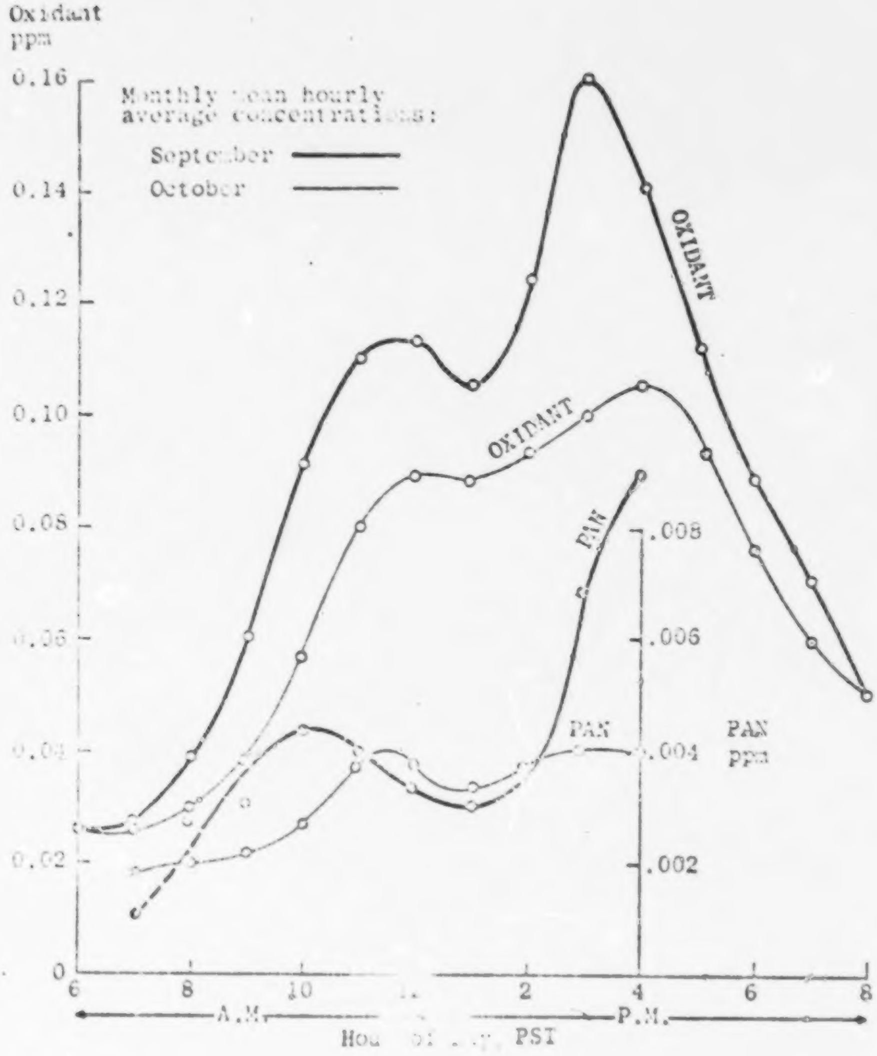


Figure 5-20. OXIDANT AND PAN CONCENTRATIONS BY HOUR OF DAY AIR POLLUTION RESEARCH CENTER--RIVERSIDE, CALIFORNIA--(1966).

Table 5-15.* AVERAGE AND MAXIMUM CONCENTRATION OF PAN - RIVERSIDE, CALIFORNIA--(AUGUST 1967-APRIL 1968).

Month	August (24-hour)	August[a] (10-hour)	Maximum (Month)
August, 1967	5.9	7.9	28
September	5.1	6.7	34
October	7.0	7.4	43
November	6.9	8.1	58
December	0.9	1.2	12
January, 1968	0.8	1.0	8
February	1.4	1.3	25
March	3.4	3.5	38
April	3.1	4.0	21

---

[a] Average for 10-hour period, 8:00 A.M. to 6:00 P.M.

* From J. APCA, 19, 348 (May 1969).

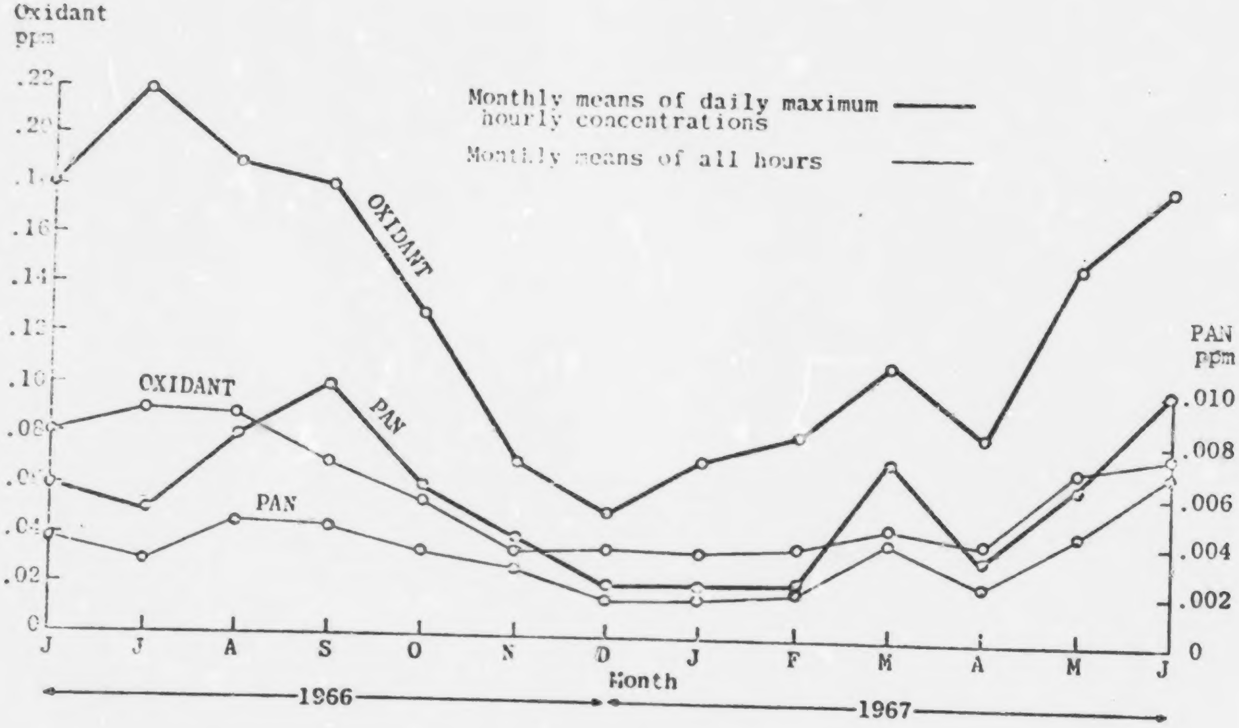
analyzer (see paragraph C.), and the average PAN concentrations are shown by hour for the month of September, 1966. Similar data for October 1966 are also shown in Figure 5-20. The monthly mean oxidant and PAN concentrations and the monthly mean of the daily maximum hourly averages are shown in Figure 5-21.

In Figure 5-20 there are two daily maxima for the oxidant and PAN concentrations. As previously discussed, the second maximum may be due to the transport of pollutants from Los Angeles to Riverside. The PAN concentrations in Riverside are an order of magnitude lower than those in Los Angeles, while the concentration of oxidants are the same order of magnitude.

Additional data have been reported recently on PAN concentrations in Riverside during late 1967 and early 1968.[114] Included was an 18-day period in November 1967 when an extended atmospheric stagnation episode resulted in the highest concentration of PAN recorded to that time. This level, 58 ppb, is still substantially lower than levels which have been observed in Los Angeles. A summary of the 1967-68 data is given in Table 5-15.

e. Aldehydes

Of all the principal reaction products formed in the atmosphere by photochemical processes, the aldehydes are among the most poorly quantified. By far most of the available data are from Los Angeles, where for the period 1951-1957 aldehydes were regularly [illegible] using manual techniques.[115] Total aldehydes were determined by the bisulfite procedure[116] and reported as formaldehyde, while formaldehyde was determined by the chromotropic acid procedure.[117] Table 5-16 shows the range of maximum concentrations obtained over this period. Typical maximum concentrations were nearer the low end of



Note: Oxidant by Mast, continouus 24 hours; PAN by Panalyzer, sequential, 0600-1600 or 1700 hours only.

Figure 5-21. OXIDANT AND PAN CONCENTRATIONS AIR POLLUTION RESEARCH CENTER--RIVERSIDE, CALIFORNIA--(JUNE 1966 THROUGH JUNE 1967, INCLUSIVE).

Table 5-16. RANGE OF MAXIMUM CONCENTRATIONS OF ALDEHYDES AND FORMALDEHYDE--LOS ANGELES COUNTY--(1951-1957).*

Year	Concentration Range (ppm)	
	Formaldehyde	Total Aldehydes
1951	.05 - .12	.26 - .67
1952		.20 - .27
1953		.25 -1.20
1954		.39 - .80
1955		.47 -1.28
1956		.51 -1.30
1957		.27 - .47

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* From "Air Quality of Los Angeles," J. E. Dickinson, Technical Progress Report, Volume II, Los Angeles County Air Pollution Control District (1961).

the range, although available data are insufficient to provide a complete characterization.

A cooperative study[118] jointly sponsored by the Air Pollution Control District of Los Angeles County and the Air Pollution Foundation during the period July-November 1960 provided limited data on total aldehydes, formaldehyde and acrolein using the bisulfite, chromotropic acid, and 4-hexybesorcinol procedures, respectively. Total aldehydes ranged up to 0.36 ppm for a 10-minute sample, while formaldehyde did not exceed 0.10 ppm. Typical aldehyde concentrations were near 0.10 ppm on many days. The maximum acrolein value was 0.011 ppm, with most values being less than half that amount.

Aldehyde concentrations tend to peak near the time of the oxidant maximum but this is not always the case, particularly in the winter season. They are produced both as primary contaminants from incomplete combustion and in the photochemical process, so that a varied diurnal and seasonal pattern is not unexpected. Because their importance has not been fully assessed and because limited sampling data are available, additional effort is necessary to determine the influence aldehydes will have in setting air quality--and hence emission--standards for photochemical reactants.

5. Trends in Photochemical Air Contaminants

The time serves analysis of air quality data involves at least four components of variation: (1) actual trends, (2) cyclical variations, (3) seasonal variations, and (4) random fluctuations. The ability to determine possible trends in air quality rests upon the extent to which cyclical, seasonal, and random variations can be accounted. The assumption generally made is that these latter three sources of variation are due to measurement and meteorological variables and that any remaining indication of trend is likely due to a real change in contaminant loading in the atmosphere.

It seems almost certain, based upon the experience of those who have examined precipitation data and other atmospheric phenomena[119], that there is an insufficient time record of photochemical air contaminant data to account for any possible long-term cycles. On the other hand there is little or no evidence of any truly cyclical behavior of any of the meteorological parameters which might affect the concentration of air contaminants.

Seasonal variations in air contaminant levels in the atmosphere are present for many contaminants and have been referred to earlier in this section. Several approaches may be used to account for this factor, the most common being the 12-month moving average. When data for several years is available, an average "seasonal index" may be calculated and applied, for example, to monthly means to obtain "deseasonalized" monthly values.

The remaining and most troublesome source of difficulty in determining possible trends is that of random variation. In the evaluation of visibility trends in Los Angeles over the period 1932 - 1958 reported by Holzworth and Maga[120] a trend of reduced visibilities was shown over the period from 1932 - 1948. Visual examination of the data suggests that the trend was not clearly established until 1940, or a period of eight years. Further evidence of the difficulty in evaluating possible trend information relating to photochemical air contaminants is shown in several figures reproduced from a report by Ingels, et al[121] on atmospheric trends of nitrogen oxides. Figure 5-22a shows a "least squares" linear trend line fitted to raw monthly data from downtown Los Angeles while Figure 5-22b shows a subjectively fitted trend curve applied to "deseasonalized" monthly data. Figures 5-23a and 5-23b show the same information for data from an air monitoring station in Burbank (about 10 miles northwest of downtown Los Angeles). Even though there was a slight increase in nitrogen oxides emissions in the County of Los Angeles during this same period, no easy interpretation of this data seems possible.

Trend data on oxidant and nitrogen dioxide for several cities in New Jersey are shown for the period 1966 - 1968 in Figures 5-24 and 5-25.[122] Although a very slight trend downward seems evident for oxidant, no significant confidence could be attached to that statement. Table 5-17 presents on a yearly basis, the maximum hourly average concentration and the number of days when the maximum hourly average for oxidant exceeded specified values at each of the CAMP sites, from 1964 through 1967.[123] Again, no evidence of trends is seen for any of the sites over the relatively short period considered.

Probably the longest time series of air quality data relating to photochemical contaminants is that from the Los Angeles County Air Pollution Control District. Figure 5-26 presents for the period 1955-1968, the yearly number of days exceeding specified levels of oxidant and nitrogen dioxide. Also shown are the number of days each year with high air pollution potential based upon the following criteria:

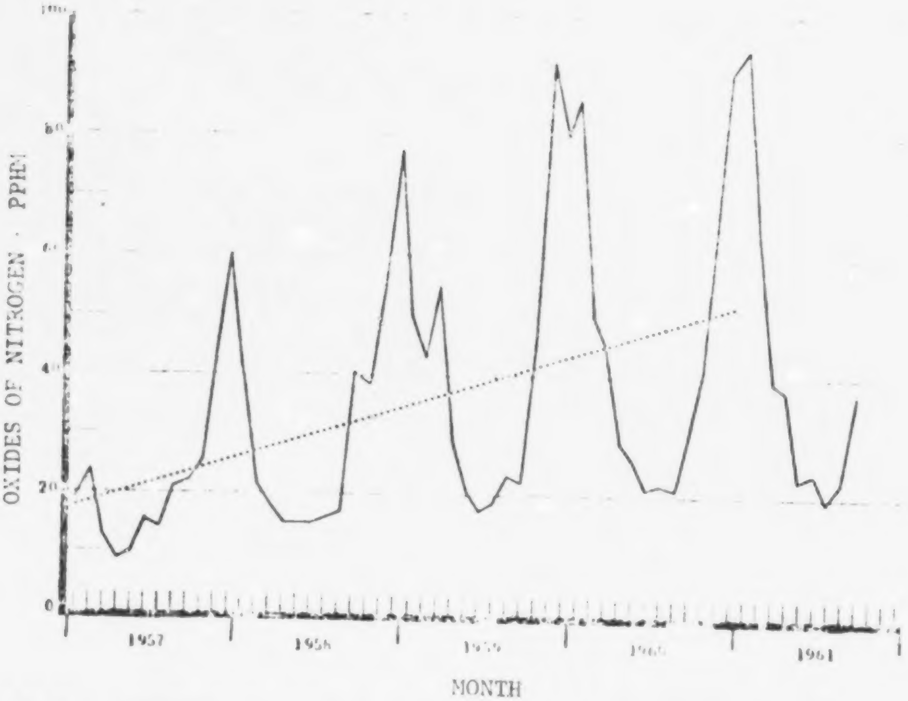

Figure 5-22a. MONTHLY MEAN DAILY MAXIMUM NO_x, CIVIC CENTER, 1957-1961. SIGNIFICANT TREND, +8.6 PPHM/YEAR.

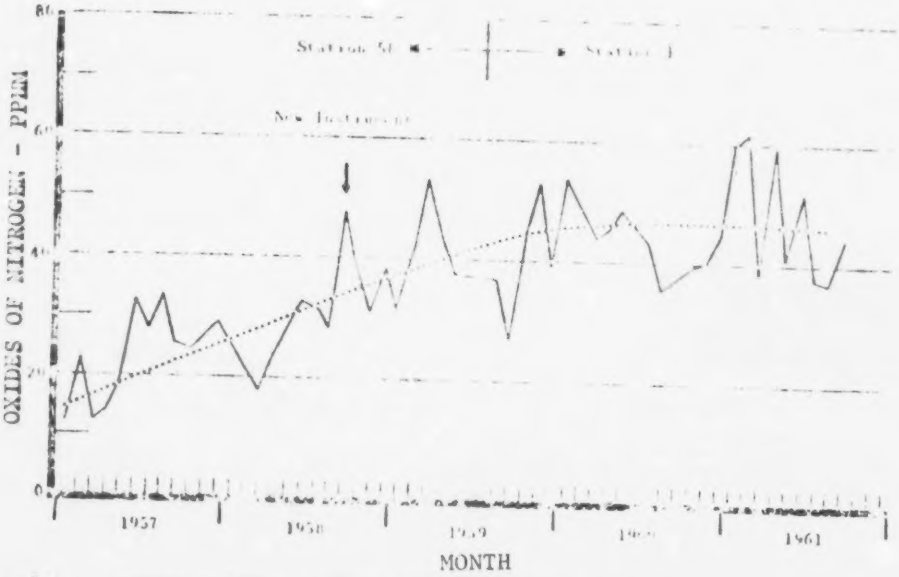

Figure 5-22b. TREND CURVES FITTED TO "DESEASONALIZED" MONTHLY MEAN DAILY MAXIMUM NO_x DATA, LOS ANGELES CIVIC CENTER, STATIONS 1 AND 58, 1957-1961.

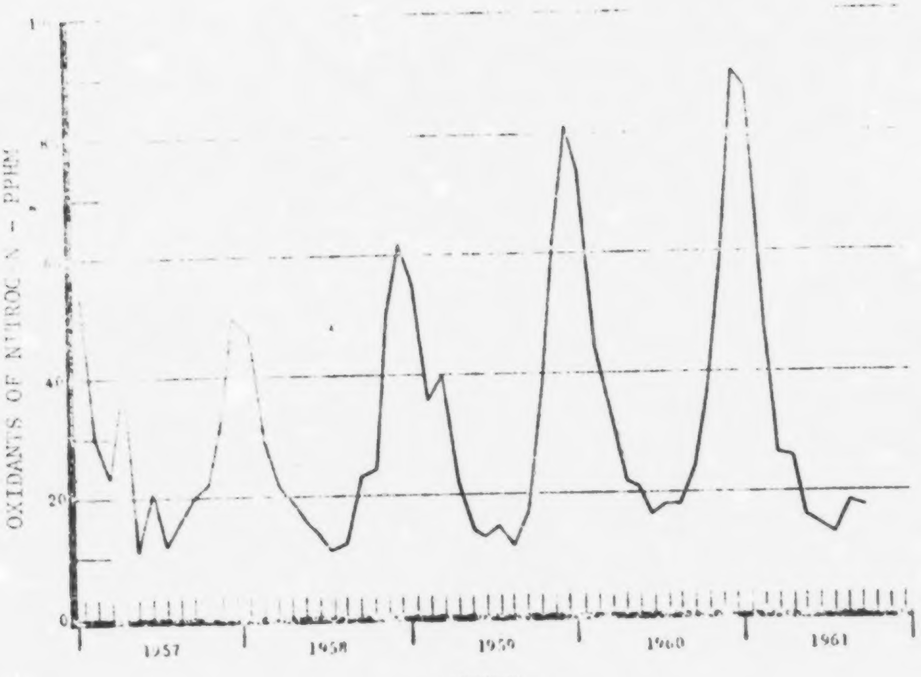

Figure 5-23a. MONTHLY MEAN DAILY MAXIMUM NO_x, BURBANK, 1957-1961. NO SIGNIFICANT TREND.

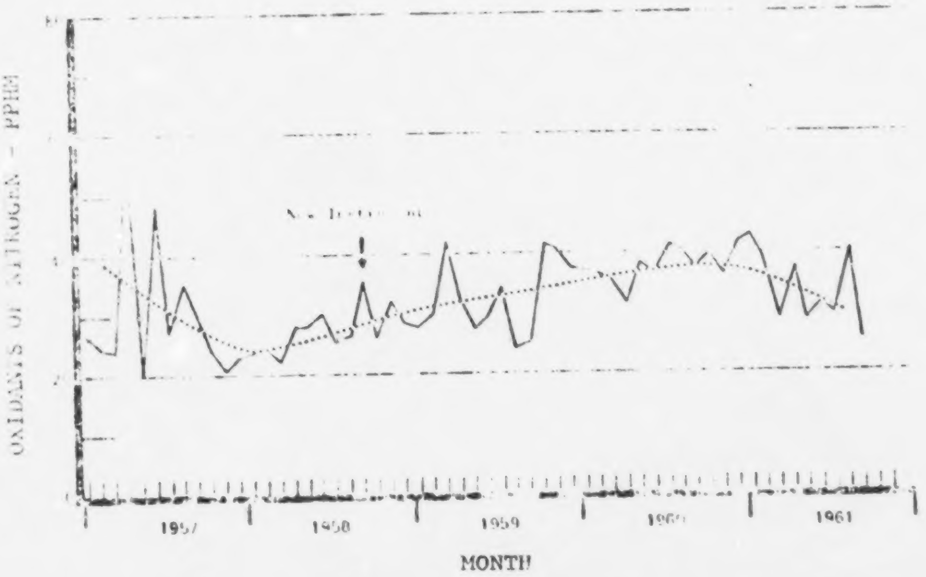

Figure 5-23b. TREND CURVES FITTED TO "DESEASONALIZED" MONTHLY MEAN DAILY MAXIMUM NO_x DATA, BURBANK, STATION 9, 1957-1961.

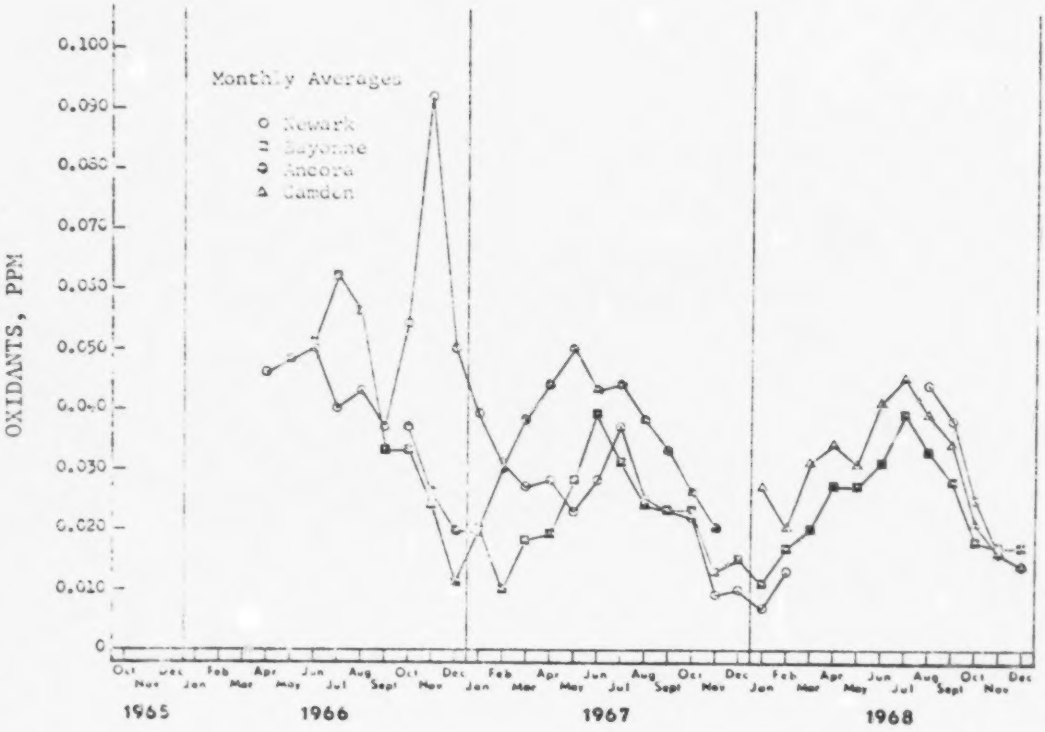

Figure 5-24. OXIDANTS.

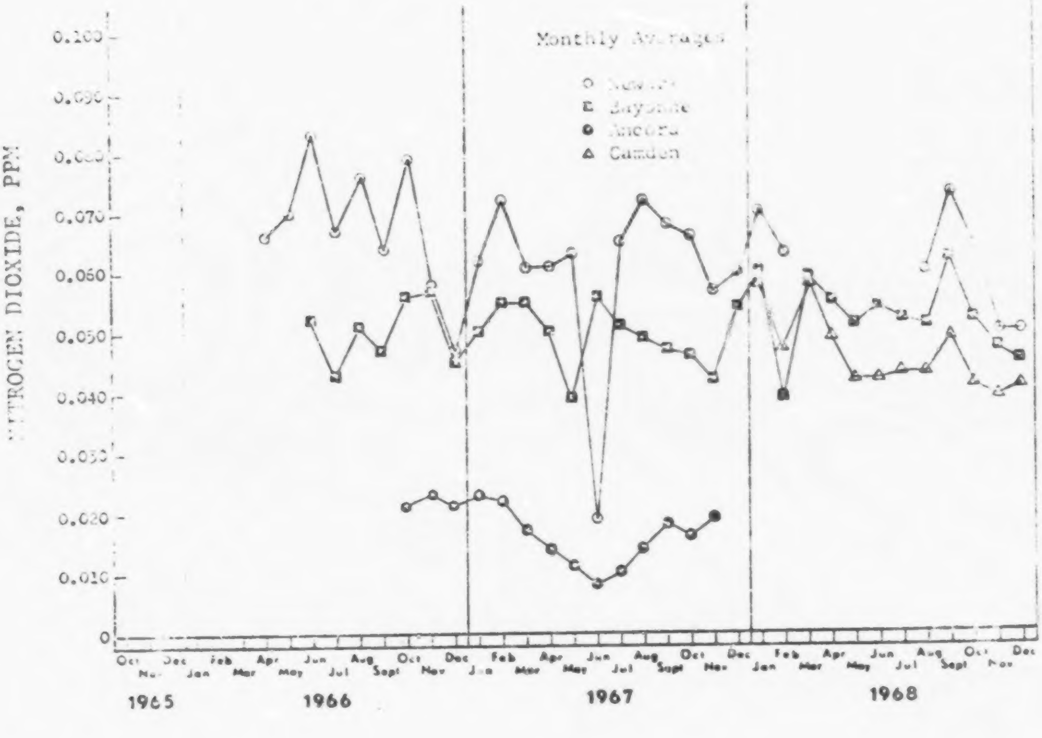

Figure 5-25. NITROGEN DIOXIDE.

Table 5-17. SUMMARY OF TOTAL OXIDANT CONCENTRATIONS RECORDED AT CAMP SITES, 1964-1967.

City	Year	Days of valid data	Number of days with at least 1 hourly average equal to or exceeding			Maximum hourly average, ppm
			0.05 ppm	0.10 ppm	0.015 ppm	
Chicago	1964	254	149	15	0	0.13
	1965	275	120	9	0	0.13
	1966	235	52	6	3	0.19
	1967	255	113	16	1	0.16
Cincinnati	1964	303	137	36	5	0.26
	1965	310	182	19	5	0.17
	1966	208	54	1	0	0.10
	1967	228	122	24	1	0.20
Denver	1965	285	226	51	14	0.25
	1966	298	187	46	9	0.19
	1967	166	76	12	4	0.21
Philadelphia	1964	269	124	37	9	0.20
	1965	266	109	23	4	0.33
	1966	315	145	52	19	0.52
	1967	282	124	28	3	0.17
St. Louis	1964	253	156	26	6	0.26
	1965	329	206	33	8	0.35
	1966	292	174	33	5	0.22
	1967	289	185	38	4	0.20
Washington, D.C.	1964	293	163	40	4	0.20
	1965	284	150	25	3	0.21
	1966	325	134	27	2	0.16
	1967	322	137	27	5	0.26

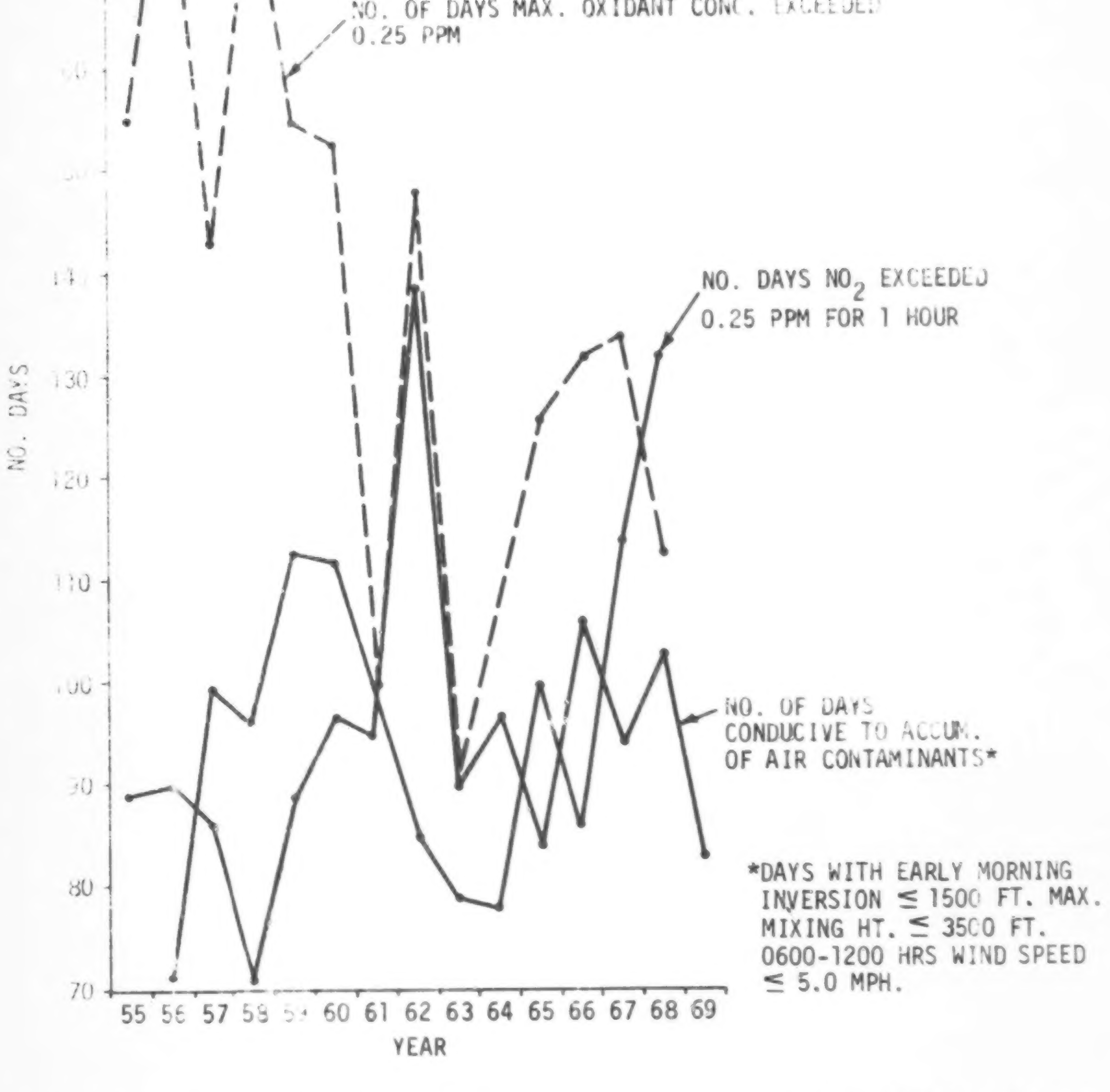

FIGURE 5-26 ANNUAL VARIATION IN NUMBER OF DAYS OXIDANT AND NO_2 EXCEED STATED LEVELS TOGETHER WITH NUMBER OF DAYS CONDUCIVE TO ACCUMULATION OF AIR CONTAMINANTS--LOS ANGELES BASIN.

1. Inversion base $\leq$ 1500 feet.
2. Maximum mixing height $\leq$ 3500 feet.
3. 0600-1200 hours average wind speed $\leq$ 5.0 mph.

A very preliminary assessment would seem to indicate a decreasing trend of days exceeding the stated oxidant level and increasing trend in number of days exceeding the given NO_2 level. It is obvious that there is substantial random, or unaccounted for, year-to-year variation. Taking the meteorological parameters as an example (for which a trend does not seem present) the standard deviation in the number of days meeting the high air pollution potential criteria is 19. This is approximately 20 percent of the mean annual value of 94 days. Several other precautions should be stated regarding the interpretation of these data. First, even though the data presented are "Basin" data (a day is included if the specified level is exceeded at any air monitoring station), there were changes in the number and location of air monitoring stations over the time period involved. Secondly, the possibility of localized influences on concentrations cannot be completely eliminated. Thirdly, it is accepted that the meteorologocal criteria used to define high air pollution potential are at best rather crude.

In summary it seems evident that really clear-cut trends in the occurrence and concentrations of photochemical air contaminants are either not present or require more powerful tools of analysis to be discerned. Serial correlation techniques normally used[124] or special tools such as power spectrum analysis as described by Brier[125] may have to be brought into play. Finally a substantial effort is still needed to account for the effects of meteorological and other photophysical influences on the reaction and accumulation of photochemical contaminants in the atmosphere.

K. DATA ACQUISITION REQUIREMENTS FOR DETERMINING REGIONAL AIR QUALITY

1. Suggested Measurements

The establishment of air quality criteria for any one of the possible air contaminants occurring as a result of photochemical reaction has significant implications insofar as atmospheric measurements are concerned. Not only must that particular contaminant be characterized so as to enable interpretation of significant expected effects, but the primary contaminants must be described in terms of those concentration parameters to permit structuring and evaluation of control implementation plans. The potential number of possible measurements is relatively great in number. This is particularly true if an atmospheric research capability is required.

For those areas in which the major objectives of an air quality data acquisition program are (1) ability to evaluate air quality against criteria and standards, and (2) ability to plan and evaluate contaminant control implementation plans, the list may be narrowed.

As a minimum, a program should involve the capability of obtaining hourly mean values for oxidant, nitrogen dioxide, nitric oxide, and hydrocarbons. It would be highly desirable to make at least some nonroutine measurements using one of the specific ozone methods to enable a more precise evaluation of the oxidant data. The potential effect of sulfur dioxide should be judged and, if necessary, compensating measures taken. If prescrubbers are necessary, the possibility of enhanced positive interference from oxidized nitric oxide should be acknowledged.

The major concern in the measurement of nitrogen oxides lies not in problems of specificity, but in development of a capability to properly calibrate and maintain presently available analyzers.

The measurement of hydrocarbons is best made on the basis of obtaining information on the reactive classes. However, this objective still remains a challenge even for research-oriented organizations having substantial laboratory resources. In lieu of obtaining detailed information on specific hydrocarbons by full gas chromatographic procedures, the method used should at least separate or remove methane from the remaining hydrocarbons. The total hydrocarbon analyzer based upon flame ionization and incorporating the accessories enabling a specific measurement of methane is, for the present, the best routine approach.

Wind speed and direction measurements will be necessary to interpret air quality data in terms of sources and to facilitate construction or estimation of overall community pollution patterns. It will be desirable in many cases to supplement the wind data available from ESSA or other sources with that collected specifically for air quality evaluation purposes.

Other measurements of photophysical parameters such as solar irradiation, vertical temperature structure and other stability parameters will be useful. It is particularly in this area that regional, State and Federal cooperation can be helpful in optimizing the utility and cost of the data.

2. Sampling Network Design

In theory, the establishment of an air sampling network should be based upon (1) criteria for meeting program objectives; (2) desired confidence in output data; (3) ability to relate sampling site measurements to sources and receptors; (4) optimizing cost/effectiveness ratios; (5) site specifications; and (6) overall program balance.

In practice, economic factors and the relative complexity of at least continuous monitoring equipment have set the pattern for the acquisition of air quality data. There has been an expansion of air sampling activity in recent years, of course, particularly in some of the major metropolitan areas mentioned in the data discussions of this chapter. But here, most of the expansion has been related to particulate and sulfur oxides measurement.

It seems prudent to assume in long-range planning of resource allocation that economic and manpower pressures will not permit the acquisition of detailed information about every point in space and time in the atmosphere. It is not, in the strictest sense, even possible to do so. It is incumbent on us then to plan future networks with strict attention to objectives, to take advantage of our knowledge of atmospheric behavior, and to apply interpretive analysis techniques to the point that our expenditures for air quality data actually contribute to the improvement in the quality of our environment.

Insofar as community air pollution is concerned we can list several principal objectives of air monitoring, as follows:

1. Establishment of background data
2. Evaluation of criteria and standards
3. Development of control strategies and plans
4. Evaluation of control programs
5. Development of acute incident warning
6. Establishment of source identification
7. Study of atmospheric transportation and chemistry.

These objectives create varying requirements for measurement time bases, sampling location density and distribution, for communications, and for total information systems. A review of a number of these factors has recently appeared.[126]

A few examples may help illustrate the applicability of some of the above factors. First, let us assume we are interested in obtaining mean geophysical contaminant levels (worldwide background). If 1000 stations were to be established, the proportionate share for the United States (based upon area) would be about 20. We would be concerned with having great measurement sensitivity and field suitability, but not necessarily with communications or immediate use of the data. Time response of the analyzer would be of little importance and sampling could very well be intermittent.

Second, we would consider the requirements for providing an early warning system against an acute incident involving the possible release of toxic material from a point source. In this case we would (1) use a very concentrated geometric sampling grid; (2) require only moderate sensitivity; (3) need rapid analyzer response; (4) use immediate communication links, and (5) demand high reliability.

The more typical community air monitoring network would fall somewhere between these extremes. The sampling grid will be affected by location of sources and receptors and by local wind patterns; some--but not all--measurements will necessitate the time response availability only from continuous analyzers. The need for systematic analysis of air sampling instrument requirements with a view towards best meeting future programs has been recognized by many. One particular scheme is illustrated by the systems chart in Figure 5-27.

In determining whether a community or air quality control region meets or exceeds air quality standards, a basic question exists as to how well any given air sampling system represents a true situation in the atmosphere. Assuming no problems with methodology, the question can be expressed in terms

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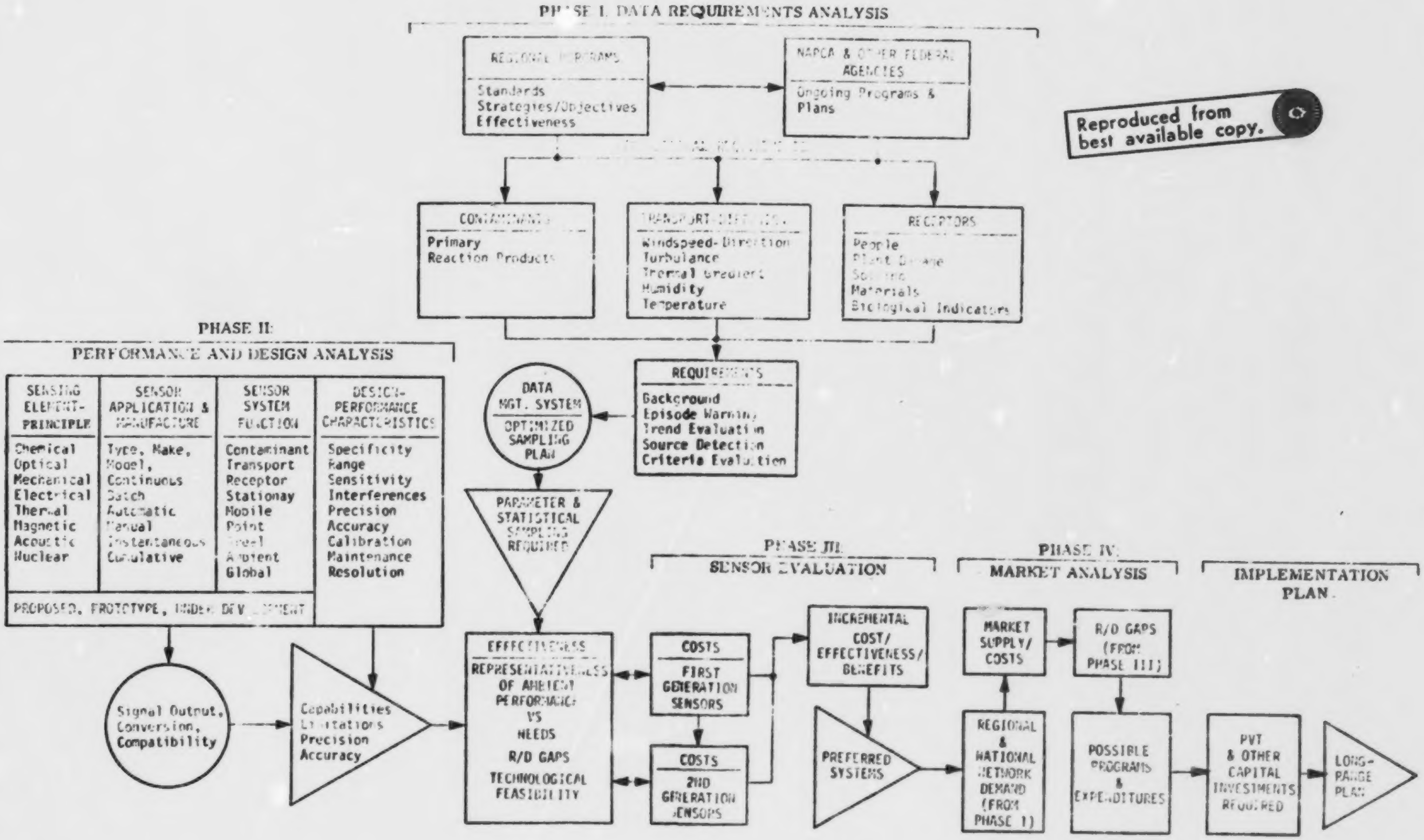

Figure 5-27. FACTORS TO CONSIDER IN THE DEVELOPMENT OF AN OVERALL AIR QUALITY APPRAISAL IMPLEMENTATION PLAN.

of the accuracy expected at a stipulated confidence level in using air quality data from a network to estimate the contaminant concentration over a given time base at a randomly selected point in time and space.

One approach to solving this problem is exemplified by the analysis by Stalker[130] of data collected as part of a large-scale epidemiological study conducted in Nashville. Up to 119 sampling site locations were used enabling the analysis of predictive approaches based upon varying numbers of stations. As a result of this work the following equation was developed to estimate the minimum number of stations required to obtain the confidence and accuracy levels specified:

$$N=(CV)^2t^2/p^2$$

where N = minimum number of stations required, t = student "t" for specified confidence interval,

CV = coefficient of variation in percent

$= \frac{\text{standard deviation}}{\text{mean}} \times 100$ (for normal distribution)

= (antilog sgx100))-100 (for lognormal distributions, where sg = standard geometric distribution), and

p = allowable departure in percent from true mean.

As an example, it was determined that 245 stations would be required (four per square mile) to estimate the daily mean concentration of SO_2 at any given point with 95 percent confidence of ± 20 percent accuracy. On the other hand it was estimated that one central and one peripheral station would be required to calculate seasonal means at any point in the area. This was based upon the finding that the geographic cross-section of values gave an approximate fit to the normal distribution curve.

A limited study[128] conducted by the Los Angeles County Air Pollution Control District using one mobile and several fixed stations showed that sampling locations up to 5 miles apart exhibited instantaneous values within ± 5 pphm of one another at all concentration levels.

Other approaches to estimating the number of sampling stations to provide a satisfactory discription of the air quality of an area are based upon atmospheric simulation models.[129] Most of these are static diffusion models and thus are not adequate to handle contaminants exhibiting significant rates of reaction over the times used in the models. Nevertheless, initial results of modeling for Connecticut[130] and several of the newly designated air quality control regions[131] indicate the possible utility of more advanced models.

One conclusion common to both the use of statistical analysis and simulation modeling techniques is that substantial field experimentation needed to develop the techniques and validate results. The potential savings and benefits possible should encourage further work in these areas.

3. Station Siting

A usual and sometimes unwarranted assumption made about air quality data is that it fairly represents a reasonable area surrounding the site. Even though we know, as discussed in the previous paragraph, that there are limits to this assumption, precautions in siting must be taken to obtain results not unduly influenced by highly localized factors.

Because physical requirements would usually preclude a purely randomized site selection procedure, the establishment of some guidelines are desirable. Factors most commonly considered can be classified as (1) external: (a) height above ground level of sampling point, (b) influence of surrounding structures or terrain on air flow, and (c) localized sources; and (2) internal: (a) length and type of sampling lines, and (b) analyzer environment.

Generally, sample inlets should be 10 to 12 feet above ground to avoid street dust from low-level turbulence and unmixed auto exhaust. Higher inlets should be evaluated in terms of atmospheric stability and representativeness of principal receptor locations. Sample locations closer than two building heights from taller structures should be avoided to preclude stagnation areas formed in the lee of such structures. Strict rules about localized source influences are difficult to define but a contribution of more than 5 percent to a measured concentration from any one source, as estimated from point source diffusion calculations, would be undesirable for a station expected to provide valid results for the surrounding area.

4. Data Processing and Validation

The usefulness of air quality data is related to its reliability and availability. The former cannot be assured only by proper method and sample location selection. Continuous attention to calibration, operation and maintenance is particularly important in continuous analyzer systems.

Calibration (the relationship of measured value to contaminant) should be carried out as specified in the description of the method being used. Neglect here can reduce to useless the value of the data collected. Operational measures such as routine zeroing and spanning, adjusting flow controls, Servicing and cleaning components, noting change in parts, and describing unusual events also contribute to [illegible] information approximating the accuracy theoretically attainable by the method.

Following the field procedures taken to produce valid information, a formal editing process is desirable for data collected with recording devices. A trained editor can detect many symptoms of malfunction such as electronic noise and component failure, which may result in drift or lack of sensitivity. Further quality control measures can be taken by establishing criteria on the acceptance or rejection of data exhibiting unusual patterns--whatever the cause--or for evidence of proper operational procedures such as entry of zero, span, flow rate and other pertinent information.

The validation procedure should continue following the reduction of data to the form used for storage. Steps would include random checks of reduced data vs. original charts and examination for rationality. Wherever computer processing is utilized some of these checks can be built into the programming. Example mean values over a given time period could be tested to insure that they be less than shorter interval means or instantaneous values over the same elapsed time. Deviation from typical patterns could be checked by flagging unusual peak-to-mean ratios or times of peaks.

Insofar as the analysis of air quality data is concerned, a prime objective is the determination of how the various indices of that data relate to criteria and standards. Most commonly these standards are expressed in terms of frequency distributions of concentration means taken over various averaging periods. Study of existing air quality data indicates that there are characteristic lognormal probability distributions functions for each contaminant at a given location. This knowledge enables the estimation of a wider range of values than actually measured. Larsen and Zimmer[132] demonstrated that 26 random 24-hour batch model nitrogen oxides samples served as a reasonably good predictor of the frequency distribution of 70,000 5-minute values taken over a period of a year with a continuous analyzer. Given the proper input, computer techniques can be used to calculate a wide variety of distribution statistics in the form required for evaluation of data against criteria and standards.

Still another use of air quality data is the development and evaluation of abatement implementation plans. One approach involves the use of atmospheric simulation models, which in turn involve emission and atmospheric diffusion and reaction submodels. Reference was made to several of these in the previous paragraph. Because these models are still in beginning stages of development, somewhat more use has been made of multivariate analysis techniques. Larsen[133] has used this approach in calculating reduced emission requirements to meet certain air quality goals for a hypothetical case.

A factor analysis approach was used by Bifford and Meeker[134] in producing a number of independent factors characteristic of certain types of pollution sources from a large amount of data on particulate subclasses from the National Air Sampling Network. A regression of these factors on the cities used in the study gave information on the importance of some of these factors in characterizing the types of pollution, and thus likely sources, in each location.

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CHAPTER 6

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A. INTRODUCTION

The purpose of this statistical analysis was to explore the interrelationships among commonly measured photochemical contaminants and meteorological variables in 7 urban regions. The year 1967 was selected for study as this was the year when the most complete data for contaminant concentration and meteorological variables were available for 12 stations in the CAMP and SCAN networks. Total oxidant concentration, an indicator of photochemical pollution, was selected as the key dependent variable. Both instantaneous daily maximum and hourly average values formed two statistical sample populations over which several types of analyses ranged.

A first iteration of the multivariate analysis was completed in four sequentially interdependent phases: (1) rank ordering of the days of the year according to the values of their peak instantaneous total oxidant concentrations; (2) frequency distribution and descriptive statistics on all hourly average photochemical contaminant concentrations and meteorological variable hourly average values; (3) correlation and regression analysis; and (4) auto and cross-correlation analysis.

B. DATA ACQUISITION AND MANAGEMENT

1. Air Quality Data

The statistical studies were concentrated on CAMP (Cooperative Air Monitoring Program) data for six cities and six Los Angeles SCAN (State of California Air Monitoring Network) stations for the year 1967, as shown in Table 1. These data were acquired from the National Air Pollution Control

TABLE 6-1 1967. PHOTOCHEMICAL AND METEOROLOGICAL DATA ELEMENTS

	Air Quality Data						Meteorological Data *						
	CO	NO	NO_2	NO_x	HC	NMHC (Methane free HC)	Wind Speed	Wind Air	Temp.	Press.	Rel. Hum.	Total Sky Cover	Mixing Height
CAMP													
Cities													
Chicago	✓	✓	✓		✓		✓	✓	✓	✓	✓	✓	
Cincinnati	✓	✓	✓		✓		✓	✓	✓	✓	✓	✓	
Denver	✓	✓	✓		✓	✓	✓	✓	✓	✓	✓	✓	
Philadelphia	✓	✓	✓		✓	✓	✓	✓	✓	✓	✓	✓	
St. Louis	✓	✓	✓				✓	✓	✓	✓	✓	✓	
Washington D.C.	✓	✓	✓				✓	✓	✓	✓	✓	✓	
Los Angeles SCAN Stations													
Anaheim	✓	✓	✓	✓	✓		✓	✓	✓	✓	✓	✓	✓
Azusa	✓	✓	✓	✓	✓		✓	✓	✓	✓	✓	✓	✓
Burbank	✓	✓	✓	✓			✓	✓	✓	✓	✓	✓	✓
Downtown L.A.	✓	✓	✓	✓	✓		✓	✓	✓	✓	✓	✓	✓
La Habra	✓	✓	✓	✓			✓	✓	✓	✓	✓	✓	✓
Pasadena	✓	✓	✓	✓			✓	✓	✓	✓	✓	✓	✓

* Meteorological data interpolated from ESSA and SCAN weather data at Los Angeles SCAN stations. See Figure 6-1.

Administration and the California Air Resources Board in the form of computer tapes. The physical and logical structure of the SCAN tapes were well described in covering documentation and were compatible to the IBM 360 series.

The CAMP information arrived on Honeywell 400 3/4 inch tapes which necessitated a complex, multistage conversion process to achieve IBM 360 compatibility.

A significant number of logical and physical tape anomalies such as variations in card image overpunching codes and an interleaving of 1968 data, not accounted for in the received covering documentation, were uncovered. A unified data storage structure and processing strategy was thus necessitated to facilitate preparation and management of CAMP and SCAN data sources. The hourly average concentration for six photochemical-related pollutants, CO, NO, NO_2, hydrocarbons, methane-free hydrocarbons (where available) and total oxidant was selected as the basic statistical unit. These data were merged with corresponding data on six meteorological variables (wind speed, wind direction, pressure, temperature, relative humidity and total sky cover).

The SCAN station variable sets were augmented by the inclusion of estimates of mixing height. The mechanics of this estimation are described below.

2. Meteorological Data

For each CAMP city and for a number of weather bureau sites in the Los Angeles basin, a directly compatible WBAN 144 deck was acquired from ESSA (Environmental Sciences Services Administration). Augmenting the

Los Angeles meteorological data, the California Air Resources Board supplied a special "dense" network data tape for six Los Angeles weather-measuring stations. These recorded the diurnal fluctuations of wind speed, direction and temperature. Computer subroutines were applied to merge these data with the pollutant data bases, thus, in effect assigning the values to the pollutant stations. For the estimation of mixing heights a series of temperature versus height radiosonde curves was constructed from Los Angeles Airport (LAX) data. Interpolated temperature is used in a computer subroutine in connection with an appropriate radiosonde curve and lapse rate to estimate the mixing height at the pollutant station. These routines are similar to those incorporated in the photochemical pollution model, described in Chapter 7.

3. Data Management

To manage the data, implement the above data transformations and place the data in a form suitable for statistical analysis, a system of original data management routines was devised. This system of programs, referred to as an Air Quality Data Management and Analysis System (AQ/DMAS), is illustrated in generalized form in Figure 6-1. AQ/DMAS, which operates on IBM 360-50-67 systems, accomplishes the following:

1. Reads Honeywell 3/4 inch tape, reproduces to 1/2 inch tape and rearranges bits to be readable on IBM 360 equipment.
2. Deciphers unique characters in Honeywell environment.
3. Transforms CAMP 5-minute-readings to correspond with other events recorded by hour or other time increments.

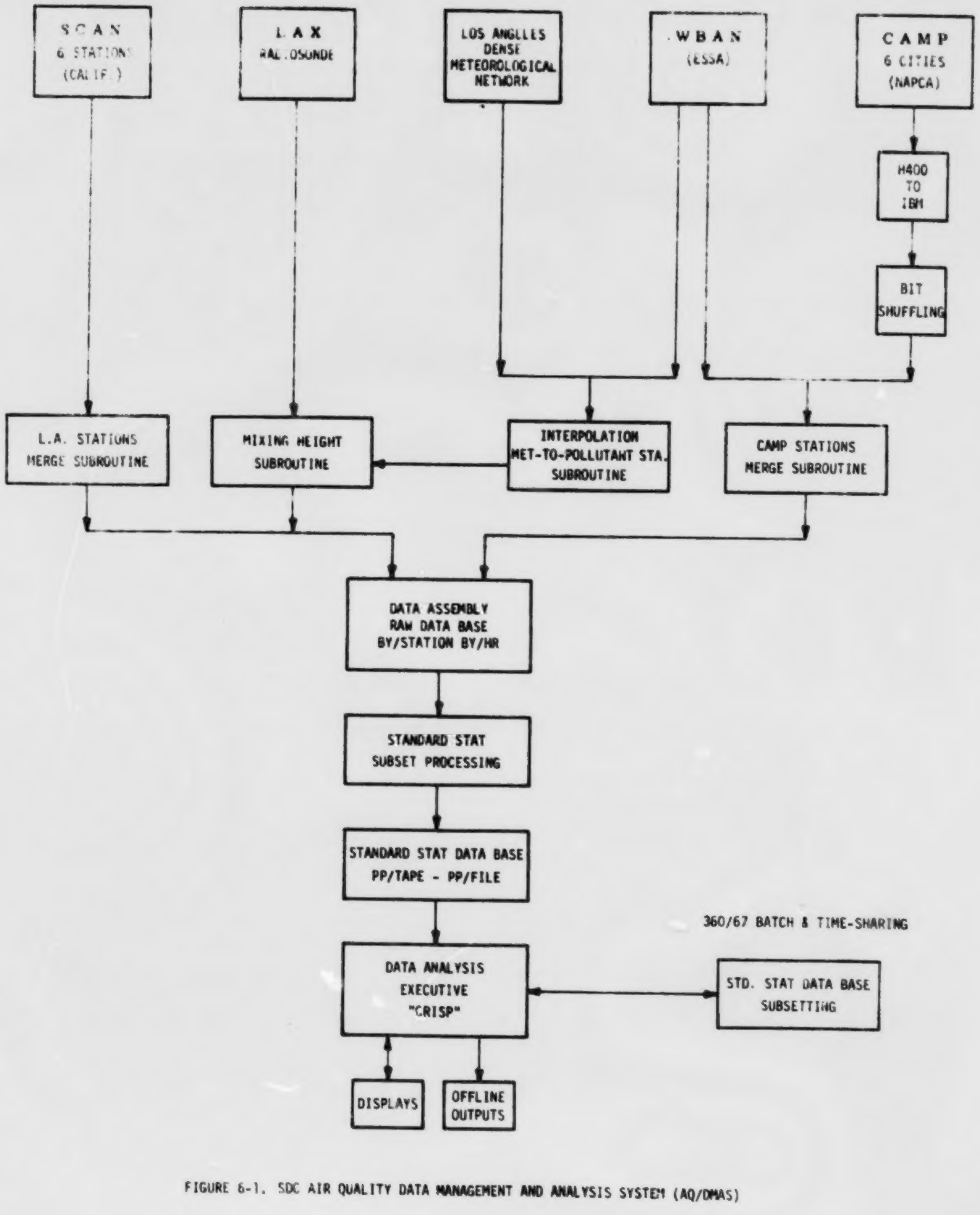

FIGURE 6-1. SDC AIR QUALITY DATA MANAGEMENT AND ANALYSIS SYSTEM (AQ/DMAS)

4. Sorts and/or reformats data to order data appropriately for station data analyses and to compensate for overpunching due to use of obsolete EAM procedures (application of machine assembly programs); places data in a guaranteed, standard format compatible with FORTRAN processing; and provides diagnostic tests and checks.
5. Interpolates meteorological data to the nearest pollutant measuring station.
6. Computes mixing height from radiosonde data.
7. Merges ESSA-WBAN and other dense meteorological data with pollutant station data (CO, HC, NO_x, SO_2, oxidant etc.), as shown in Figure 6-2.
8. Provides data retrieval, extraction, subsetting and format capabilities.
9. Provides standard statistical data base files, and performs statistical analysis desired. Programs used include rank order, descriptive statistics, frequency distributions, auto- and cross-correlations, multiple regression, contingency tables and others.

C. THE STATISTICAL PROGRAM SYSTEM

The format of the merged pollutant/meteorological pre-processed data file tapes was designed to be directly accessible, via appropriate structured control card decks, to a library of statistical programs. These included the following:

```
TEC:371 STIPROCS ON OCI

EVERY 11TH HR, CAMP, DENVER
  HOUR    MONT     DAY     HOUR    CARB     NITR     NITR     SULF     TOTA     TOTA     METH     NON-     WIND     WIND     STAT     TEMP     RELA     TOTA
   OF      H                       ON M     IC O     OGEN     UR D     L HY     L OX     ANE      METH      DIR      SPE      ION      ERAT     TIVE     L SK
  YEAR                             ONOX     XIDE      DIO     IOXI     DROC     IDAN              ANE      ECTI     ED,K     PRES     URE,      HUM     Y CO
                                   IDE               XIDE      DE      ARB.      T               HYDR      ON      NOTS     SURF     D.F.      ID.     VER
   11.00    1.00    1.00   10.00    5.00     9.00     5.00     0.0 *********    1.00******************     0.0      0.0    24.34    39.00    41.00     0.00
   22.00    1.00    1.00   21.00   12.00    10.00     4.00*********    31.00    1.00******************  350.00    10.00    24.34    33.00    39.00     0.30
   33.00    1.00    2.00    8.00    4.00     2.00     3.00*********    19.00    1.00******************  220.00     7.00    24.55    24.00    84.00     1.00
   44.00    1.00    2.00   19.00    5.00     3.00*********     0.0 *********    1.00******************  180.00     7.00    24.71    18.00    96.00     0.10
   55.00    1.00    3.00    6.00    3.00******************     1.00************************************  190.00    12.00    24.59    14.00    46.00     0.0
   66.00    1.00    3.00   17.00    9.00*********     3.00     1.00************************************  300.00    14.00    24.54    44.00    31.00     0.90
   77.00    1.00    4.00    4.00    5.00     4.00     4.00     1.00*********    1.00******************  180.00     3.00    24.60    23.00    65.00     0.0
   88.00    1.00    4.00   15.00   11.00     4.00     3.00     1.00*********    2.00******************  310.00    10.00    24.63    52.00    26.00     0.30
   99.00    1.00    5.00    2.00    3.00     1.00     2.00     1.00************************************  190.00     9.00    24.65    38.00    44.00     0.70
  110.00    1.00    5.00   13.00   11.00     2.00     3.00     1.00*********    5.00******************  350.00     5.00    24.71    59.00    21.00     0.40
  121.00    1.00    6.00    0.0     4.00     7.00     4.00******************    3.00******************   90.00     4.00    24.12    25.00    71.00     0.10
  132.00    1.00    6.00   11.00******************************************************************  310.00    10.00    24.39    30.00    26.00     0.30
  143.00    1.00    6.00   22.00    6.00*********     3.00     1.00************************************  310.00     6.00    24.55    18.00    24.00     0.20
  154.00    1.00    7.00    9.00    7.00*********     4.00     1.00************************************  150.00     8.00    24.70     4.00    54.00     0.0
  165.00    1.00    7.00   20.00    5.00     9.00     4.00     5.00*********     0.0 ******************  190.00     9.00    24.80    11.00    44.00     0.0
  176.00    1.00    8.00    7.00    3.00     2.00     3.00     1.00*********    1.00******************  200.00    13.00    24.73    14.00    33.00     0.70
  187.00    1.00    8.00   18.00    9.00     3.00     4.00     1.00*********    1.00******************   70.00     5.00    24.75    34.00    30.00     1.00
  198.00    1.00    9.00    5.00    8.00*********     5.00     1.00************************************     0.0      0.0    24.88    19.00    69.00     0.70
  209.00    1.00    9.00   16.00   20.00     9.00     5.00******************    2.00******************  100.00     7.00    24.95    34.00    41.00     0.70
  220.00    1.00   10.00    3.00    5.00     6.00     4.00     1.00    27.00    1.00******************  200.00     4.00    25.03    23.00    59.00     0.70
  231.00    1.00   10.00   14.00   13.00******************     1.00    24.00    5.00******************   80.00     8.00    24.99    55.00    29.00     0.90
  242.00    1.00   11.00    1.00*********     3.00     3.00     1.00    17.00    2.00******************  180.00    13.00    24.85    37.00    48.00     0.0
  253.00    1.00   11.00   12.00   24.00    15.00     6.00*********    61.00***************************  200.00    11.00    24.69    59.00    20.00     0.50
  264.00    1.00   11.00   23.00   10.00     5.00     4.00     0.0     32.00    1.00******************  130.00     9.00    24.67    37.00    37.00     0.60
  275.00    1.00   12.00   10.00   13.00******************     0.0     46.00    1.00******************   10.00     5.00    24.55    39.00    49.00     1.00
  286.00    1.00   12.00   21.00   13.00     9.00     3.00     0.0     37.00    1.00******************  190.00     8.00    24.43    29.00    75.00     0.30
  297.00    1.00   13.00    8.00   19.00    13.00     5.00     0.0     50.00***************************     0.0      0.0    24.45    27.00    58.00     0.60
  308.00    1.00   13.00   19.00    7.00     2.00     2.00     0.0     19.00    3.00******************  300.00    20.00    24.50    46.00    34.00     0.20
  319.00    1.00   14.00    6.00    4.00     2.00     3.00     0.0     19.00    2.00******************  360.00    11.00    24.55    25.00    81.00     0.70
  330.00    1.00   14.00   17.00    6.00     4.00     3.00     0.0     22.00    3.00******************   50.00     8.00    24.75    25.00    56.00     1.00
  341.00    1.00   15.00    4.00    3.00     2.00     4.00     0.0     18.00    1.00******************  140.00     9.00    24.51    15.00    88.00     0.30
  352.00    1.00   15.00   15.00   15.00     2.00    11.00     3.00    43.00    7.00******************  180.00     5.00    24.55    40.00    73.00     0.90
  363.00    1.00   16.00    2.00    7.00     0.0      0.0      0.0     10.00***************************  210.00     8.00    24.41    49.00    42.00     0.60
  374.00    1.00   16.00   13.00    9.00***************************    22.00***************************   40.00     4.00    24.65    32.00    66.00     0.90
  385.00    1.00   17.00    0.0     4.00     7.00     3.00     0.0     22.00    1.00******************  160.00     5.00    24.92    23.00    96.00     1.00
  396.00    1.00   17.00   11.00    9.00     5.00     4.00     0.0     19.00    4.00******************  180.00    14.00    24.94    26.00    48.00     0.30
  407.00    1.00   17.00   22.00    5.00     3.00     4.00     0.0     22.00    2.00******************  330.00     9.00    24.75    12.00    96.00     1.00
```

Figure 6-2. SAMPLE OF TOTAL MERGED DATA BASE, DENVER, 1967. Includes CAMP station variables, and corresponding hourly WBAN variables. This specimen gives every 11th hour reading for review purposes.

1. Rank Order Analysis

A rank order subroutine was developed and applied to identify "high oxidant" episode days, in order to reduce the possibility of dealing with data which do not reflect actual photochemical activity. The subroutine ranked days by decreasing levels of average oxidant, peak oxidant, average NO_2 and peak NO_2, and gave the month and day of all values and the hour the peak values occurred. This subroutine was applied to each of the 12 air monitoring stations being studied and served, along with the frequency distribution, as the criteria for the selection of days for more detailed statistical analyses. A sample Rank Order Analysis is shown in Figure 6-3.

Days were selected primarily on the basis of the peak instantaneous value of total oxidant concentration which was greater than or equal to a prespecified value. The value selected was 7 pphm for the CAMP Cities (Chicago, Cincinnati, Denver, Philadelphia, Washington, D.C., and St. Louis) and 14 pphm for the Los Angeles SCAN Stations (Anaheim, Azusa, Burbank, Downtown Los Angeles, La Habra and Pasadena.)

2. Frequency Distribution and Simple Statistics

Frequency distributions and simple statistics were computed for each data element defined in Table 6-1 at each station. Each such frequency distribution consists of a table of observed frequency versus the numerical value of the variable. The sample statistics are, for each variable, sample number, mean, standard deviation, low and high. Figure 6-4 is an example of the frequency distribution table for hourly average total oxidant concentration

RANK	AVERAGE OXIDANT (PPHM)			PEAK OXIDANT (PPHM)			AVERAGE NO (PPHM)			PEAK NO2 (PPHM)		
	DAY LEVEL	24-HR LEVEL	MONTH /DAY	PEAK LEVEL	PEAK HOUR	MONTH /DAY	DAY LEVEL	24-HR LEVEL	MONTH /DAY	PEAK LEVEL	PEAK HOUR	MONTH /DAY
1	11	11	6/ 5	16	12	9/ 9	24	17	4/ 6	63	6	9/ 7
2	9	8	6/ 3	14	15	6/ 5	23	16	1/24	52	7	8/29
3	8	8	6/26	14	13	7/21	22	14	11/16	52	7	9/ 9
4	7	7	5/11	13	23	5/17	20	17	1/14	49	23	5/17
5	6	6	1/24	12	17	1/24	20	20	4/ 3	44	8	11/16
6	5	6	6/ 4	12	15	6/ 3	20	14	12/28	43	8	4/ 6
7	6	6	9/ 7	11	13	9/ 2	19	11	4/14	39	8	1/ 4
8	5	5	5/17	11	15	9/ 4	18	13	1/ 4	37	8	3/13
9	5	5	5/31	11	15	6/14	16	12	1/25	37	1	4/14
10	5	5	6/14	11	9	7/11	18	13	3/13	36	21	1/22
11	5	5	6/20	11	15	8/ 2	19	14	4/ 2	34	9	4/16
12	5	5	6/28	11	7	11/11	18	15	12/10	34	5	9/ 2
13	5	5	6/29	10	8	1/14	18	13	12/15	34	7	12/28
14	5	5	7/11	10	23	3/11	17	13	12/ 9	33	8	12/30
15	5	5	9/ 8	10	22	5/11	17	12	12/30	32	8	4/14
16	5	5	9/ 9	10	13	6/ 7	16	16	1/19	32	23	3/26
17	5	5	9/18	10	15	7/22	16	12	3/14	31	23	3/11
18	5	5	9/19	10	6	4/29	16	12	3/15	31	22	10/22
19	5	5	10/ 2	10	5	9/ 7	16	12	3/17	31	9	11/11
20	5	5	10/31	10	20	10/31	16	11	3/29	30	7	1/25
21	4	4	1/14	9	7	1/25	15	10	1/12	30	15	4/14
22	4	4	3/ 3	9	23	4/16	15	9	2/23	30	18	12/ 7
23	4	4	3/ 9	9	13	4/22	15	14	3/ 3	29	15	1/24
24	4	4	3/11	9	15	5/ 6	15	10	3/ 7	29	16	4/17
25	4	4	3/13	9	16	5/26	15	9	3/20	29	6	4/28
26	4	4	4/27	9	9	9/ 3	15	11	4/ 7	29	7	8/12
27	4	4	5/ 9	9	15	9/ 9	15	11	4/19	28	9	4/ 2
28	4	4	5/10	8	12	6/23	15	10	8/11	28	22	6/26
29	4	4	5/12	8	13	7/17	15	10	9/ 9	28	4	8/11
30	4	4	5/14	8	16	9/13	15	10	11/ 4	27	11	1/19
31	4	4	5/29	8	20	10/20	15	10	12/12	27	8	3/29
32	4	4	5/30	8	15	11/10	14	9	2/28	27	8	4/19
33	4	4	6/ 2	7	20	1/22	14	9	5/12	27	1	4/25
34	4	4	6/ 6	7	9	3/ 2	14	13	11/10	27	21	5/10
35	4	4	6/ 7	7	19	3/ 3	14	9	11/11	27	17	12/11
36	4	4	6/ 8	7	14	3/12	13	10	1/ 3	26	16	3/16
37	4	4	6/15	7	16	4/13	13	13	1/13	26	8	3/17
38	4	4	6/30	7	19	4/17	13	9	3/ 6	26	7	3/22
39	4	4	7/17	7	16	5/ 9	13	10	3/ 6	26	9	11/ 8
40	4	4	7/21	7	13	5/10	13	9	4/22	26	16	6/13

Figure 6-3. RANK ORDER ANALYSIS, ANAHEIM, 1967. This subroutine ranks days by decreasing levels of oxidant, and NO_2, in order to identify "episode days" on which concentrated analysis is subsequently performed.

```
VARIABLE  10      FREQ.     PERCENT OF TOTAL     PERCENT OF NON-BLANKS          TOTAL OXIDANT
 40.00000           2               0.02                0.02    100.00
 39.00000           1               0.01                0.01     99.98
 38.00000           1               0.01                0.01     99.96
 36.00000           8               0.09                0.10     99.95
 35.00000           3               0.03                0.04     99.85
 34.00000           3               0.03                0.04     99.82
 33.00000           5               0.06                0.06     99.78
 32.00000          10               0.11                0.12     99.72
 31.00000           8               0.09                0.10     99.60
 30.00000          10               0.11                0.12     99.50
 29.00000          12               0.14                0.15     99.38
 28.00000          12               0.14                0.15     99.23
 27.00000          21               0.24                0.26     99.09
 26.00000          17               0.19                0.21     98.83
 25.00000          30               0.34                0.37     98.62
 24.00000          32               0.37                0.39     98.26
 23.00000          28               0.32                0.34     97.87
 22.00000          34               0.39                0.41     97.53
 21.00000          58               0.66                0.71     97.12
 20.00000          55               0.63                0.67     96.41
 19.00000          54               0.62                0.66     95.74
 18.00000          50               0.57                0.61     95.08
 17.00000          75               0.86                0.91     94.47
 16.00000          71               0.81                0.86     93.56
 15.00000          80               0.91                0.97     92.70
 14.00000          86               0.98                1.05     91.72
 13.00000         112               1.20                1.36     90.68
 12.00000         124               1.42                1.51     89.31
 11.00000         113               1.29                1.38     87.80
 10.00000         130               1.48                1.58     86.43
  9.00000         120               1.37                1.46     84.84
  8.00000         156               1.78                1.90     83.38
  7.00000         194               2.21                2.36     81.49
  6.00000         201               2.29                2.45     79.12
  5.00000         326               3.72                3.97     76.68
  4.00000         433               4.94                5.27     72.71
  3.00000         719               8.21                8.75     67.44
  2.00000        1450              16.55               17.65     58.69
  1.00000        3371              38.48               41.03     41.03
 BLANK            545               6.22

 NON-BLANK       8215       MEAN #      4.56677      STANDARD DEVIATION #     5.92210
```

Figure 6-4. FREQUENCY DISTRIBUTION FOR TOTAL OXIDANT.

measured at the Pasadena SCAN station. Figure 6-5 is a statistical summary of all pollutant and meteorological variables measurements (or computed estimates) at the SCAN station located at the U.S.C. medical school.

3. Correlation and Regression Analysis

A multiple regression analysis program was applied to the data for high-oxidant days for each station (high oxidant days defined by the episode criteria mentioned previously, namely, oxidant 14 pphm or higher at SCAN stations and 7 pphm or higher at CAMP stations). In this application, the dependent variable was related to maximum hourly oxidant, while the independent variables were based on concurrent and immediately preceding values of contaminants (CO, NO, NO_2, total hydrocarbon, non-methane hydrocarbon) and of weather parameters (wind speed, pressure, temperature, relative humidity, sky cover and mixing height).

Logarithmic indices were used, rather than the directly observed values, on the premise that frequency distributions for these variables tend to be lognormal rather than normal. Further, in empirical studies relating to variables of this type it is common to use power-law relations and multiplicative combinations, both of which are compatible with linear regressions on the corresponding logarithmic indices, but not with linear regressions on the direct values. The dependent variable was taken as the common logarithm of the daily maximum hourly average oxidant, while each of the independent variables was the mean logarithm of three observed values, viz., the hourly average value for the hour of maximum oxidant and the hourly average values for the two hours

```
                                   PHOTOCHEMICAL PROJECT, SCAN AND SYNTH WEATH,SCHEDSCHL,1967
NO OF VARIABLES      18
TOTAL SAMPLE SIZE 8760

                       VAR     N          MEAN          STD DEV            LOW             HIGH
HOUR OF YEAR             1  8760     4380.50000      2528.93851      0.100000 01      0.876000 04
MONTH                    2  8760        6.52603         3.44805      0.100000 01      0.120000 02
DAY                      3  8760       15.72055         8.79675      0.100000 01      0.310000 02
HOUR                     4  8760       11.50000         6.92258      0.0              0.230000 02
CO           PPM         5  8505        1.73051         3.26892      0.500000 01      0.320000 02
NO           PPHM        6  7133        5.95065         6.96478      0.100000 01      0.610000 02
NC2          PPHM        7  7119        7.11842         5.58572      0.100000 01      0.480000 02
SO2          PPHM        8     0        0.0             0.0          0.100000 39     -0.100000 39
HC-TOTAL     PPMC        9  8295        3.16335         1.39220      0.100000 01      0.120000 02
OXIDANT      PPHM       10  7918        3.38343         4.61762      0.100000 01      0.400000 02
NOX          PPHM       11  7041       13.12186        10.52528      0.200000 01      0.840000 02
MIX.HT.      METERS     12  5098      979.27442       730.67371      0.137000 03      0.817600 04
WIND DIR.    DEG.       13  8749      191.94285        95.00734      0.450000 02      0.360000 03
WIND SPD.    KNOTS      14  8760        5.05297        11.08990      0.100000 01      0.270000 03
BAR.PRESS.INS.          15  8760        0.0             0.0          0.0              0.0
TEMPERATURE(F)          16  5117       65.02501        10.92689      0.200000 01      0.990000 02
REL.HUM.     %          17  8760        0.0             0.0          0.0              0.0
CLCUDCOVER(0-1)         18  8760        0.0             0.0          0.0              0.0
```

Figure 6-5. DESCRIPTIVE STATISTICS.
Descriptive statistics for U.S.C. Medical School, 1967 air monitoring data. Synthetic weather refers to meteorological values interpolated to this pollutant station from the nearest weather station in the "dense" SCAN met network. Mixing height, in meters, is computed by means of special subroutines applied to radiosonde data.

immediately preceding the hour of maximum oxidant. In effect, the question being tested was whether maximum oxidant as observed on days of high oxidant could be related in a statistical sense to other contaminants and weather parameters taken as multiplying factors.

As illustrated in Figure 6-6 and 6-7, the program generated regression coefficients and related statistics for the entire set of independent variables, then identified the best subsets of the independent variables for all possible subset sizes and performed equivalent computations for these best subsets. Coefficients of correlation between the dependent variable and each of the independent variables were also generated.

Results are discussed in more detail in subsequent paragraphs. They showed, however, that in every case a subset of three independent variables could be found for which the regression was significant at the 5 percent level or below.

4. Auto-correlation and Cross-correlation

In auto-correlation, a set of values of a variable is arranged in chronological sequence, and two series of values are obtained by taking initial values for two different starting times, each followed by all successive members of the same sequence. Auto-correlation is the determination of coefficients of correlation between such series of values, and the difference in starting times of the two series is termed "lag". A value near +1 indicates that the difference between values in the sequence, separated by the specified lag, is ordinarily small relative to the range covered by all the values in the sequence; that is,

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```
                    CHICAGO-67 ,SELECTED ON OXMAX,LOG10,AVERAGED(0,-1,-2)

SAMPLE SIZE_____NO OF INDEPENDENT VARS_____DEPENDENT VARIABLE__________ITERATIONS
   58                      9                         10                          142

                     VARIABLE       MEAN         STANDARD         CORR WITH       STD PARTIAL         REGRESSION
                                                 DEVIATION         DEP VAR        REGR COEFF          COEFFICIENT
CARBON MONOXIDE          1        0.83300        0.28656          0.35765        -0.13124           -0.45734D-01
NITRIC OXIDE             2        0.79863        0.42210          0.11172        -1.2296            -0.29132
NITROGEN DIOXIDE         3        0.79726        0.19563          0.32561         0.19536            0.10524
TOTAL HYDROCARB.         4        1.5979         0.13943          0.38916         1.3176             0.94593
WIND SPEED,KNOTS         5        0.88778        0.19852         -0.26080        -0.78832D-01       -0.39711D-01
STATION PRESSURE         6        1.4572         0.26493D-02      0.16833        -0.12294           -4.6059
TEMPERATURE,D.B.         7        1.7263         0.11207          0.11171        -0.41674           -0.37188
RELATIVE HUMID.          8        1.7944         0.13056         -0.97423D-01    -0.13611           -0.10425
TOTAL SKY COVER          9       -0.23088        0.25839         -0.78950D-01     0.33969            0.13146
TOTAL OXIDANT           10           0.94982        0.10000                      Y INTERCEPT   =      7.31681

STANDARD ERROR OF ESTIMATE        0.08816
SHRUNKEN MULT. CORR. COEFF.       0.48851               SOURCE          SS         DF       MS          F       P
COEFFICIENT OF DETERMINATION      0.34550             REGRESSION      0.19694      9.     0.02168     2.815 0.97017D-02
MULTIPLE CORR. COEFFICIENT        0.58779             DEVIATIONS      0.37308     48.     0.00777
                                                           TOTAL      0.57002
```

Figure 6-6. REGRESSION ANALYSIS OF EPISODE DAYS SELECTED ON BASIS OF RANK ORDER ANALYSIS.

```
                                        Subset Size 2
FINAL SET OF VARIABLES       STD PARTIAL REGR COEFFS       REGRESSION COEFFS      Y INTERCEPT =    0.11827      25 ITERS.
NITRIC OXIDE        2               -0.54120                   -0.12822
TOTAL HYDROCARB.    4                0.82006                    0.58815

STANDARD ERROR OF ESTIMATE        0.08765                  SOURCE          SS       DF       MS          F        P
SHRUNKEN MULT. CORR. COEFF.       0.49541              REGRESSION      0.14745      2.    0.07372     9.595 0.26628D-03
COEFFICIENT OF DETERMINATION      0.25667              DEVIATIONS      0.42257     55.    0.00768
MULTIPLE CORR. COEFFICIENT        0.50659                   TOTAL      0.57002


                                          SUBSET SIZE  3

FINAL SET OF VARIABLES       STD PARTIAL REGR COEFFS       REGRESSION COEFFS      Y INTERCEPT =    0.29926      60 ITERS.
NITRIC OXIDE        2               -0.80015                   -0.19957
TOTAL HYDROCARB.    4                0.97560                    0.69971
TEMPERATURE,D.B.    7               -0.19266                   -0.17210

STANDARD ERROR OF ESTIMATE        0.08786                  SOURCE          SS       DF       MS          F        P
SHRUNKEN MULT. CORR. COEFF.       0.49217              REGRESSION      0.15318      3.    0.05106     6.615 0.68973D-03
COEFFICIENT OF DETERMINATION      0.26873              DEVIATIONS      0.41684     54.    0.00772
MULTIPLE CORR. COEFFICIENT        0.51839                   TOTAL      0.57002


                                          SUBSET SIZE  4

FINAL SET OF VARIABLES       STD PARTIAL REGR COEFFS       REGRESSION COEFFS      Y INTERCEPT =    0.41432      80 ITERS.
NITRIC OXIDE        2               -0.76629                   -0.19159
NITROGEN DIOXIDE    3                0.14359                    0.07734
TOTAL HYDROCARB.    4                0.88893                    0.64407
TEMPERATURE,D.B.    7               -0.25202                   -0.22489

STANDARD ERROR OF ESTIMATE        0.08785                  SOURCE          SS       DF       MS          F        P
SHRUNKEN MULT. CORR. COEFF.       0.49257              REGRESSION      0.16102      4.    0.04026     5.216 0.12831D-02
COEFFICIENT OF DETERMINATION      0.28248              DEVIATIONS      0.40900     53.    0.00772
MULTIPLE CORR. COEFFICIENT        0.53149                   TOTAL      0.57002
```

Figure 6-7. REGRESSION ANALYSIS OF EPISODE DAYS SELECTED ON BASIS OF RANK ORDER ANALYSIS.

that a high value is relatively more likely to be followed by another high value than by a low one. A coefficient near zero, on the other hand, indicates that a high value is as likely to be followed by a low value as by a high one, while a value near -1 suggests that a high value is much more likely to be followed by a low value than by a high one.

When applied to hourly contaminant data or weather data, high auto-correlation coefficients show that hour-to-hour changes in the measurement under study are usually of smaller amplitude than the diurnal cycle as a whole.

To provide sequences of hourly contaminant data for auto-correlation analysis, the output of the rank-order analysis for each station was scanned and periods of three or more successive days of high maximum oxidant were identified. As an example, the four days from June 2 through June 5 provided such a period for the Chicago CAMP station; the output of the auto-correlation program is shown in Figure 6-8. Lags of one hour to five hours were studied, for each of four contaminants. At lag of one hour, coefficients for nitrogen dioxide and oxidant were near 0.9, while those for nitric oxide and hydrocarbons were near 0.7. At lag of three hours, nitrogen dixide and oxidant coefficients were near 0.5, while nitric oxide and hydrocarbons were near zero. This sort of behavior is probably to be attributed to the status of nitric oxide and hydrocarbons as primary contaminants, more subject to rapid change because of relatively small shifts in wind direction or in community activity from hour to hour, while the accumulation or dissipation of the secondary contaminants, nitrogen dixoide and oxidant, is relatively insensitive to these shifts.

```
                    LAG =  0  LAG =  1  LAG =  2  LAG =  3  LAG =  4  LAG =  5
NITRIC OXIDE        1.00000   0.66830   0.31973   0.06870  -0.08080  -0.04651
                   (    82)  (    76)  (    72)  (    71)  (    68)  (    66)
NITROGEN DIOXIDE    1.00000   0.85984   0.69410   0.50386   0.35474   0.24330
                   (    88)  (    82)  (    78)  (    78)  (    77)  (    75)
TOTAL HYDROCARB.    1.00000   0.67151   0.31930   0.07735  -0.06614  -0.13681
                   (    95)  (    93)  (    92)  (    91)  (    90)  (    89)
TOTAL OXIDANT       1.00000   0.89566   0.72911   0.54407   0.35883   0.23462
                   (    69)  (    61)  (    58)  (    56)  (    53)  (    51)
```

Figure 6-8. AUTO-CORRELATIONS. Correlations with hourly lag-time (Chicago CAMP Station, 1967).

(In fact, records of continuous monitoring of these contaminants frequently show rapid changes in nitric oxide concentrations near peak traffic hours.)

In six other episodes at various CAMP and SCAN stations, the same auto-correlation behavior was found for oxidant, with coefficients for lag 1 hour ranging from 0.85 to 0.93.

Cross-correlation refers to the determination of coefficients of correlation between levels of different pollutants taken in corresponding time sequence, with or without the introduction of lag. Thus with hourly values for two contaminants, the existence of a coefficient near +1 suggests that the diurnal variation of the two is quite similar, while a coefficient near -1 suggests that they vary in reciprocal fashion.

D. RESULTS AND DISCUSSION

The statistical analysis completed in this project represents, in effect, a first exploratory iteration on the data. The primary objectives were to: (1) identify photochemical pollution episode days; (2) explore the ability of the contaminants and meteorological variables to account for photochemical pollution episodes, as measured by oxidant; and (3) establish the relationships that exist among oxidant, hydrocarbons, NO and NO_2. Analyses (1) and (2) were undertaken first in order to identify and validate the sample populations of interest. Analyses were also conducted for (3) in the form of correlation, regression and some contingency studies, the results of which are reported in this chapter. However, in view of the extensive analyses which are now possible on the established data bases, this analysis is less than exhaustive. It is also incomplete with respect to the SCAN network, as five of the eleven stations were not included in this study.

The station-by-station results of these analyses are described in the Appendix I of this document. A summary of the results are shown in Table 6-2 and the following.

1. The SCAN Stations as a Set

With respect to information obtained by rank-order analysis, the six Los Angeles SCAN stations studied exhibit a good deal of similarity. For SCAN stations the modal months of peak instantaneous oxidant concentration episodes are July, August, and October. Peak instantaneous oxidant concentrations are most apt to occur during the time interval between the 10th and 15th hours with probabilities of around .90. For all the stations the modal value of observed oxidant total hourly average concentration is 1 pphm.

Yearly mean values range from a low of 2.84 pphm for La Habra to 5.4 for Azusa. The range of interstation observation data variability may be characterized by a sample standard deviation low of 3.94 pphm for Anaheim to a sample standard deviation high of 7.12 pphm for Azusa. More detailed study of the relative levels of the contaminants at the SCAN stations yielded information bearing on some proposed hypothesis or generalizations as to the relations between contaminants, and their geographical variations.

Frequency distributions of the hourly values of all variables were generated for six of the eleven SCAN stations: Anaheim, Azusa, Burbank, Los Angeles (DOLA), La Habra, and Pasadena. Non-blank values were available for oxidant, carbon monoxide, nitric oxide, nitrogen dioxide for more than 85

	Peak Oxidant	Hour of Peak	High Oxidant Days, Number	Mode of Peak Oxidant Hour	Average Oxidant Mean	Standard Deviation	Mode	Low	High	Main Month of Episodes	Peak NO_2 for Maximum OX Day	Hour of Peak NO_2	Number of Days NO_2 Exceeds Peak	Days of High Oxidant, %	Best Correlated Independent Variable	Coefficient of Correlation
	PPHM					PPHM					PPHM			b	c	
SCAN																
Anaheim	43	13	113	14	3.46	3.94	1	0	37	10	17	9	36	3.2	3	.30
Azusa	73	12	204	14	5.40	7.12	1	0	65	8	15	8	55	10.0	1	.60
Burbank	5[illegible]	12	182	12	4.64	6.18	1	0	47	7,8	42	8	12	9.7	1	.48
Los Angeles	45	13	144	11	3.35	4.15	1	0	36	8	41	23	15	4.0	3	.30
La Habra[a]	31	14	54	13	2.84	3.95	1	0	29	10	24	16	5	2.9	10	-.50
Pasadena	53	12	189	13	4.57	5.92	1	0	40	7	13	7	134	9.3	10	-.59
CAMP																
Chicago	16	12	58	15	2.93	2.93	2	0	16	6	52	7	1	5.0	4	.39
Cincinnati	19	13	68	15	3.14	3.14	2	0	20	9	10	23	89	5.1	8	-.21
Denver[a]	20	10	48	9,13	2.82	2.82	2	0	21	8	8	7	124	2.9	2	-.31
Philadelphia	17	16	81	11,12	2.63	2.63	2	0	17	7	6	6	256	5.5	3	.25
St. Louis	20	14	119	12	3.44	3.44	2	0	20	7	6	6	223	6.0	5	-.46
Washington	25	1	79	12	2.57	2.57	2	0	26	7	76	1	3	6.0	1	.48

NOTE: a. Data incomplete for La Habra and Denver.

b. For SCAN, OX ≥ 14 pphm; for CAMP, OX ≥ 7 pphm.

c. Variables: 1, CO; 2 NO; 3, NO_2; 4, HC; 5, wind speed; 6, pressure; 7, temperature; 8, humidity; 9, sky cover; 10, mixing height (not in set for CAMP).

Table 6-2. SAMPLE STATISTICS, ALL STATIONS, 1967.

percent of the 8,760 hours of the year (1967) for all stations except La Habra; at the latter station, nitric oxide was known for less than 15 percent of the year. Total hydrocarbon levels were available for more than 85 percent of the year for Anaheim, Los Angeles and Pasadena, and for 25 percent of the year for Azusa, but were missing throughout the year for Burbank and La Habra. These frequency distributions (except for La Habra) are depicted in Figures 6-9 through 6-13, showing values of the 50, 75, 90, 95 and 99 percentiles, and the highest value, of the cumulative distribution of each contaminant, derived from computer output tables of the type illustrated in Figure 6-4.

As illustrated in Figure 6-9, oxidant levels at Azusa exceeded those at the other four stations at all percentiles above the 75th. Oxidant levels at Burbank were appreciably lower, and those at Pasadena still lower. Lowest were levels at Los Angeles and Anaheim, which were nearly equivalent throughout. (From the fragmentary data of La Habra, not shown, levels there appeared slightly lower than those of Anaheim and Los Angeles). Figures 6-10 through 6-13 show that Azusa levels for the other contaminants were in each case either lowest or near the lowest among the five stations. From this it may be concluded that a relatively high frequency of occurrence of high levels of the primary traffic related contaminants is not required in order to produce a relatively high level of development of photochemical oxidant at a given location, even within a single air quality region such as the Los Angeles Basin.

A concise overview of the relative levels of these contaminants at the five stations is shown in Table 6-3, which shows the rankings of the stations in order of descending values of the 99th percentile, for each contaminant.

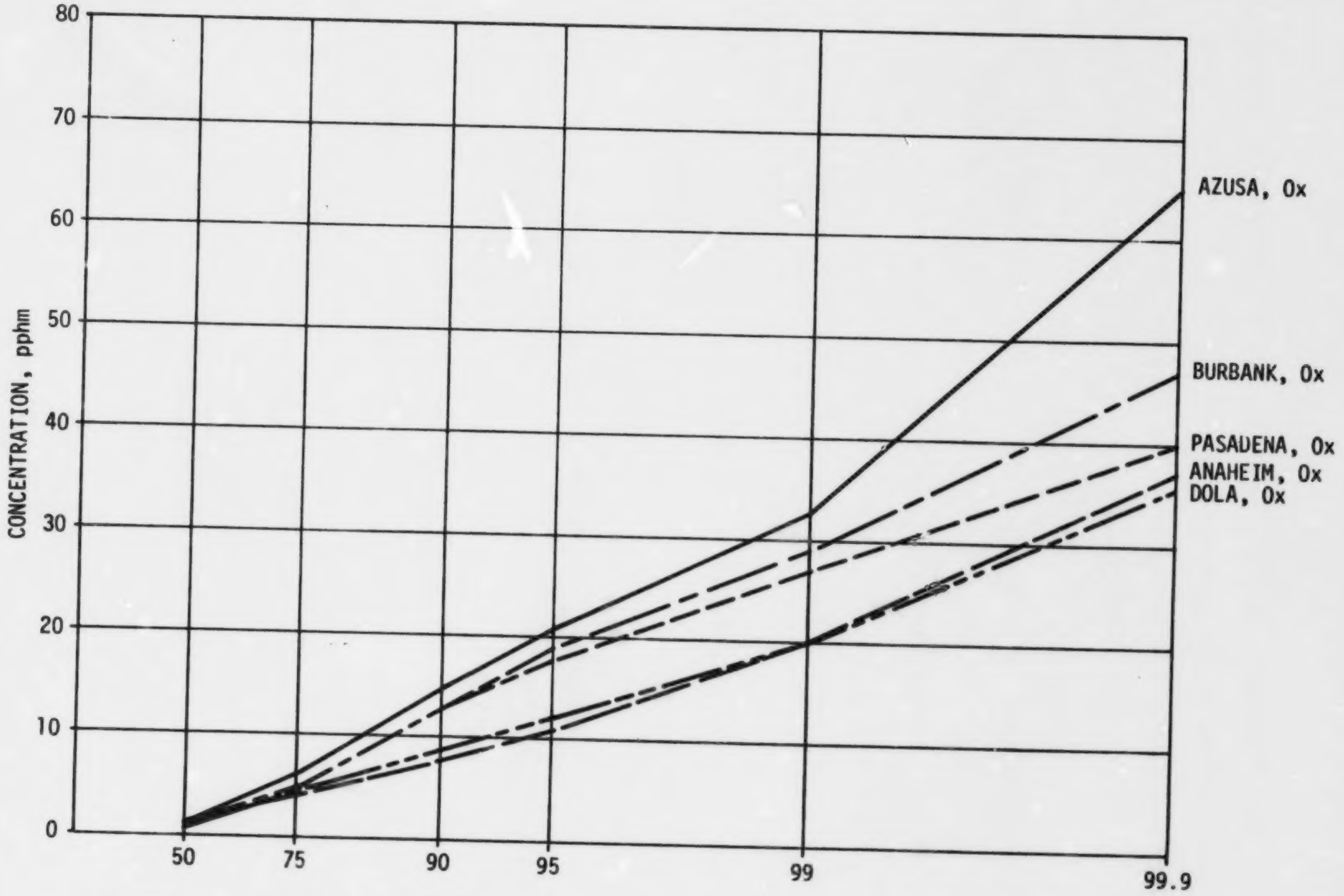

FIGURE 6-9. CUMULATIVE FREQUENCY DISTRIBUTIONS OF HOURLY AVERAGE OXIDANT, 1967, 5 SCAN STATIONS

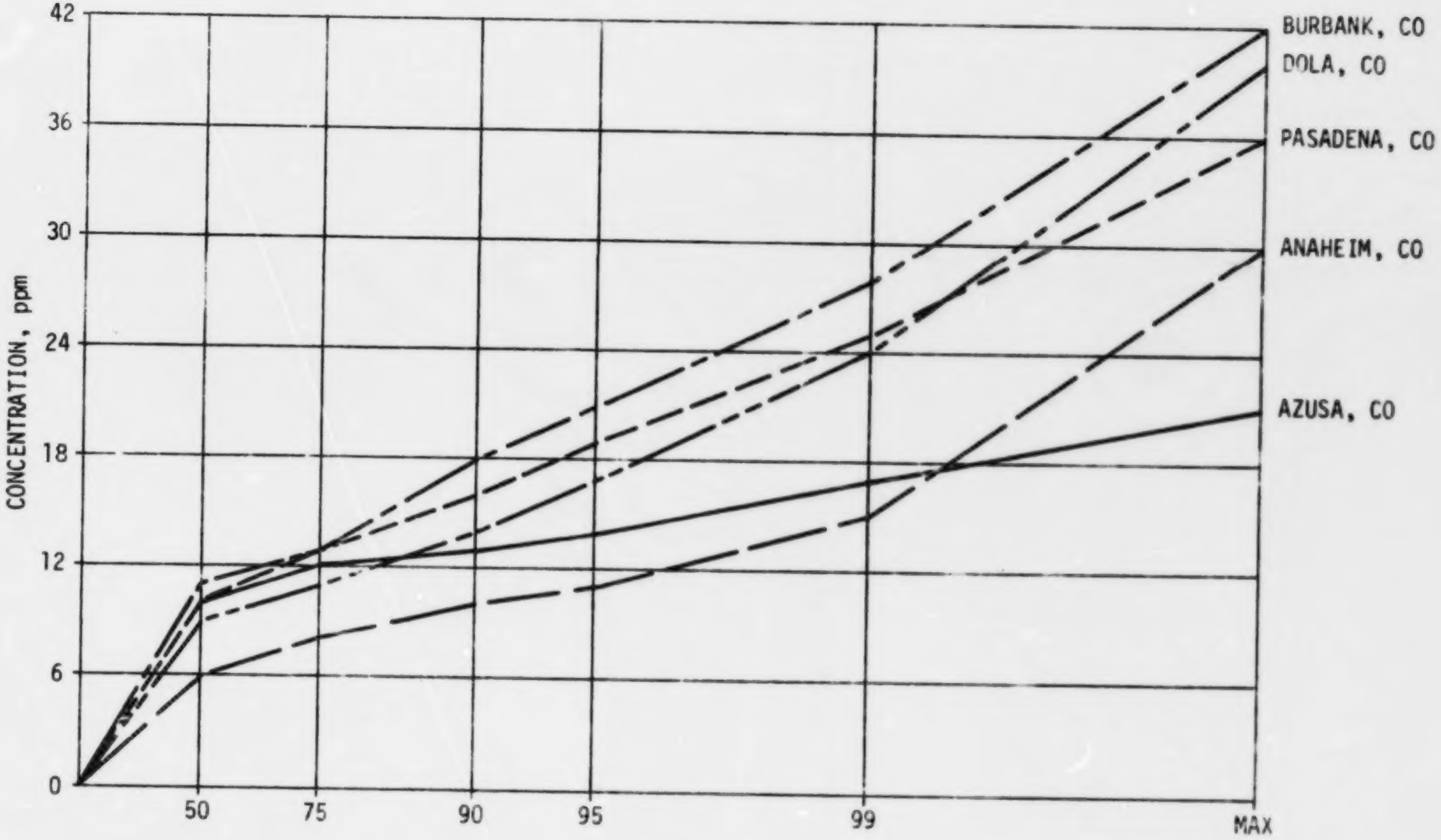

FIGURE 6-10. CUMULATIVE FREQUENCY DISTRIBUTIONS OF HOURLY AVERAGE CARBON MONOXIDE, 1967, 5 SCAN STATIONS

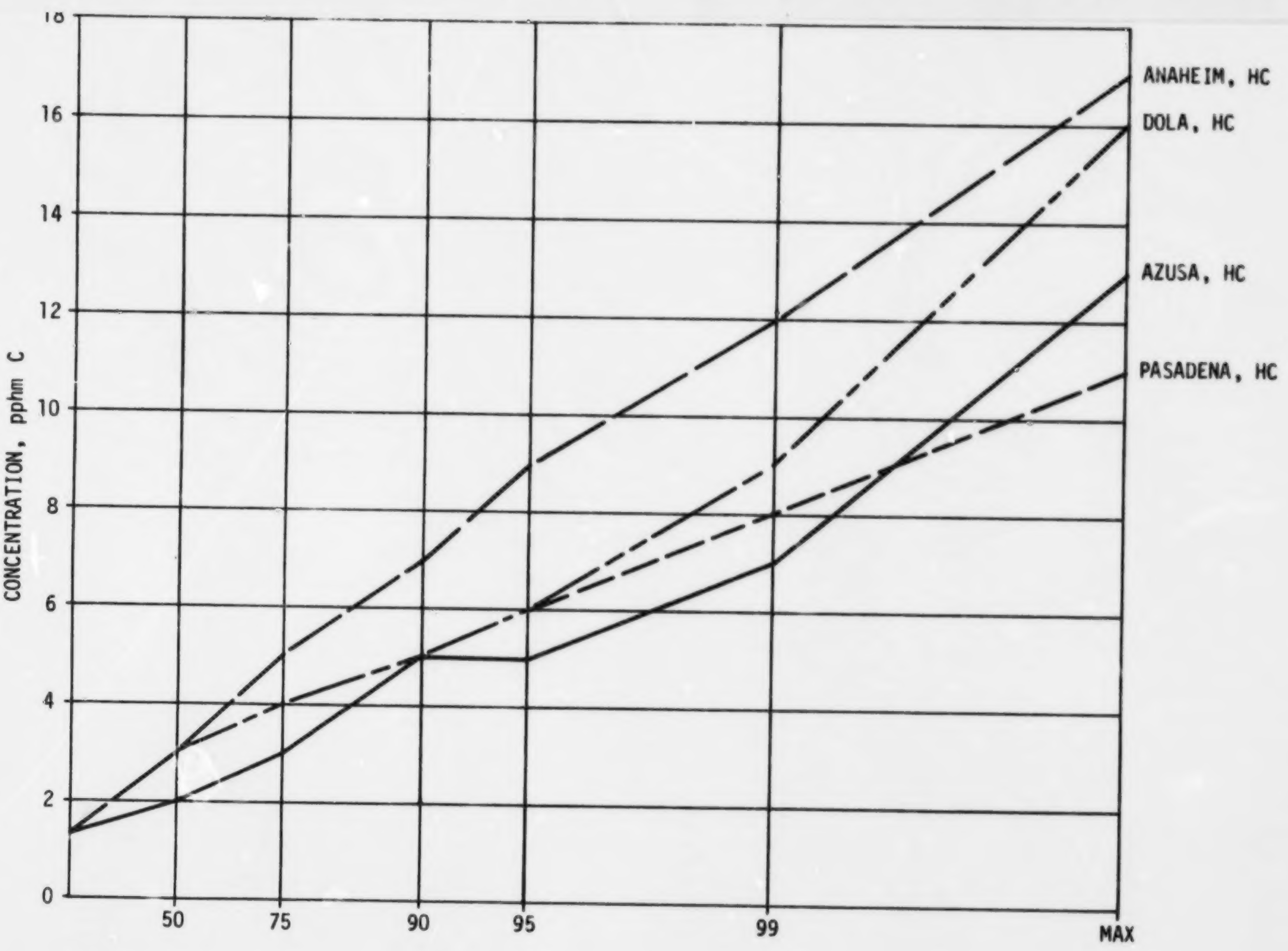

FIGURE 6-11. CUMULATIVE FREQUENCY DISTRIBUTIONS OF HOURLY AVERAGE TOTAL HYDROCARBONS, 1967, 4 SCAN STATIONS

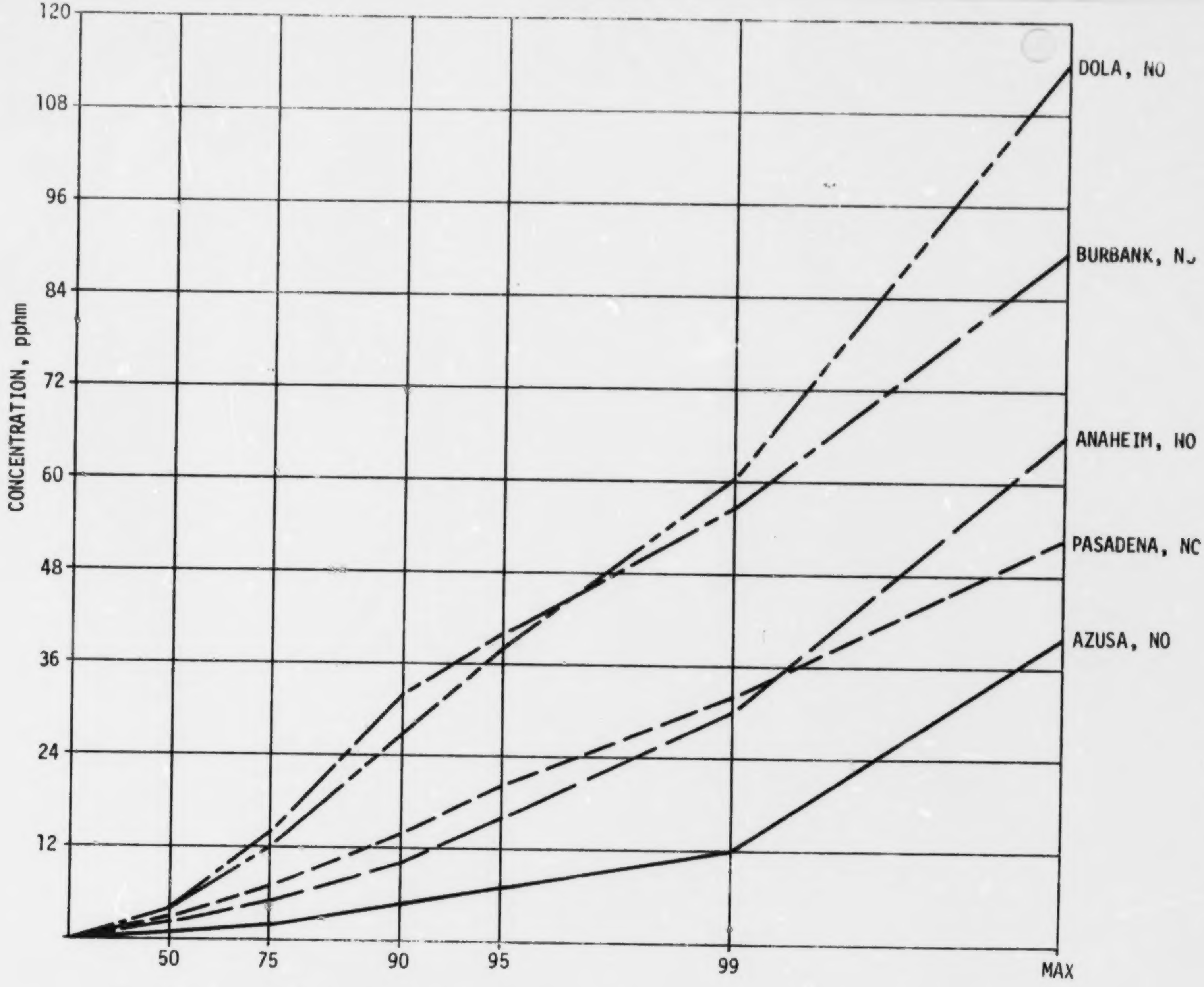

FIGURE 6-12. CUMULATIVE FREQUENCY DISTRIBUTIONS OF HOURLY AVERAGE NITRIC OXIDE, 1967, 5 SCAN STATIONS

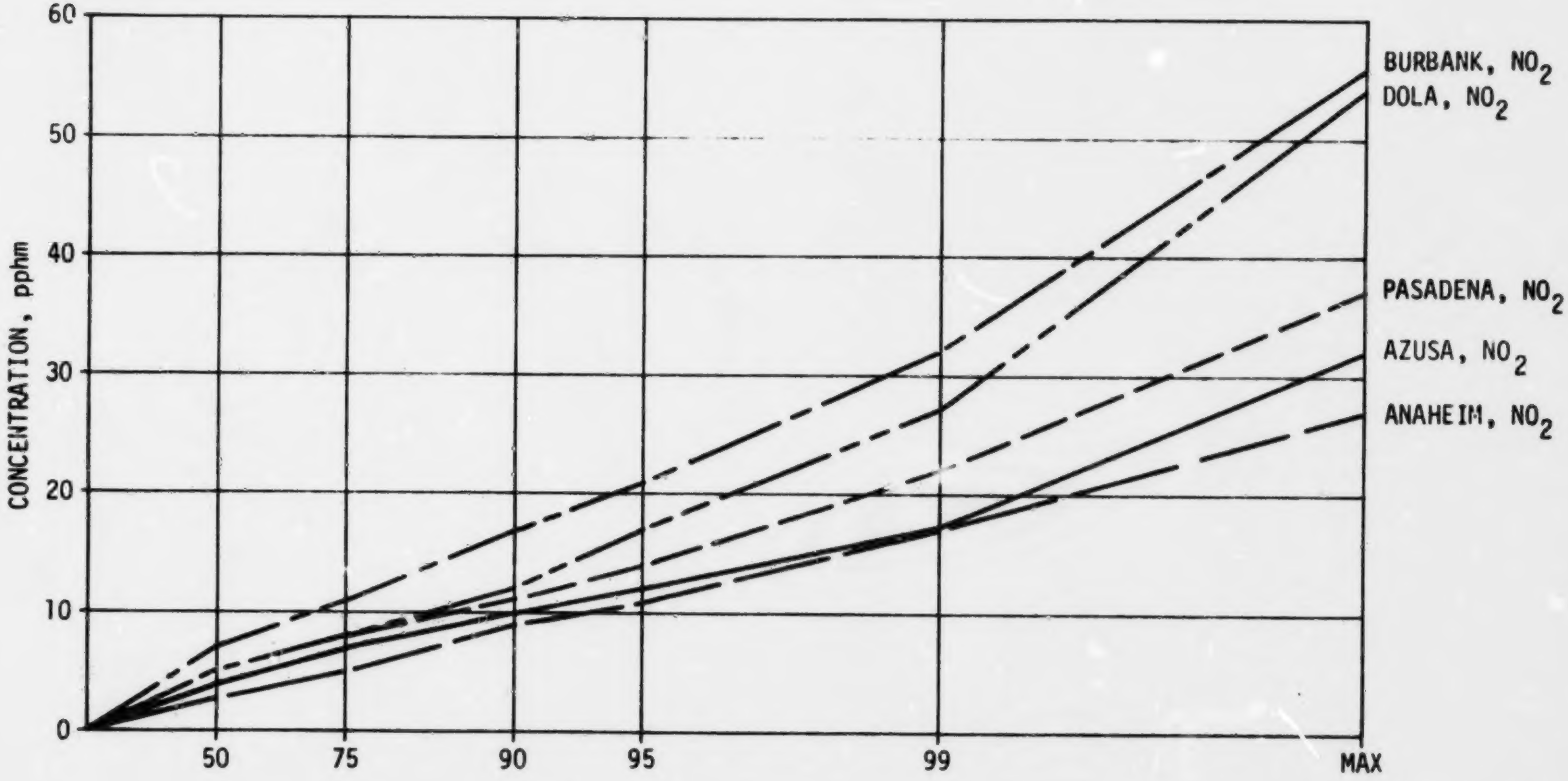

FIGURE 6-13. CUMULATIVE FREQUENCY DISTRIBUTIONS OF HOURLY AVERAGE NITROGEN DIOXIDE, 1967, 5 SCAN STATIONS

Table 6-3. COMPARISON OF FIVE SCAN STATIONS BY RANKING RELATIVE TO FIVE CONTAMINANTS (99th PERCENTILE)

	Ox	CO	HC	NO	NO_2
Azusa	1	4	5	5	4
Burbank	2	1	(1)	2	1
Pasadena	3	2	4	3	3
Los Angeles	4	3	3	1	2
Anaheim	5	5	2	4	5

(With respect to hydrocarbons, Burbank is tentatively assigned the first ranking on the basis of its high levels of traffic gas constituents as indicated by carbon monoxide; this assignment is uncertain, however, in view of the lack of complete agreement in rankings on these two contaminants at the remaining stations).

When these rankings are compared, it is seen that there is reasonable agreement (parallelism) between carbon monoxide and nitric oxide; between carbon monoxide and nitrogen dioxide, and between nitric oxide and nitrogen dioxide. On the other hand, there is poor agreement or none between other pairs of contaminants, and there is substantial disagreement (antiparallelism) between oxidant and nitric oxide rankings.

Some particularly interesting examples of disagreement (i.e., anomalies in terms of a hypothesis of parallelism in contaminant rankings) are the following:

(1) Azusa had highest oxidant but lowest HC and NO, and low CO and NO_2.

(2) Anaheim had high hydrcarbons but lowest CO, Ox and NO_2, and low NO.

(3) Burbank had highest CO, NO_2 and (probably) HC, but only second highest Ox.

(4) Los Angeles and Anaheim, although having low and very similar oxidant levels, had widely different levels of NO and NO_2.

This brief listing of important discrepancies, in effect, suffices to demonstrate that annual air quality with respect to photochemical oxidants at a selected location within the Los Angeles Basin cannot be readily deduced from a knowledge only of the annual levels of the primary contaminants at that point. As a corollary, predicting the oxidant levels at a selected location requires consideration of the daily history of air arriving at that location, that is, history in terms of the sources of primary contaminants that accumulate in it, and the reactions that take place between them while the air is en route to the selected location. For this it is necessary to consider the real paths of motion of the air - an approach which is implemented in the photochemical environmental simulation model, described in Chapter 7.

Correlation and regression results are summarized in Table 6-4. Of the 9 or 10 independent variables available, carbon monoxide yielded the highest individual correlation with the dependent variable (maximum hourly average oxidant) at two stations, Azusa and Burbank; coincidentally, these are the two stations for which oxidant levels were highest, as discussed above. For two other stations, nitrogen dioxide yielded the highest correlation; for the remaining two stations mixing height was more strongly correlated with oxidant than was any other contaminant. In the best subset of three variables, mixing height appeared for five of the six stations, with Los Angeles the only station for which this was not true. Temperature appeared in three of the six best subsets of three, and carbon monoxide appeared in the same three. Nitrogen dioxide appeared in two, as did relative humidity; nitric oxide, pressure, and sky cover appeared in one each.

It is interesting that the best subset of three independent variables proved to be identical (carbon monoxide, mixing height, and temperature) for the

Table 6-4. RESULTS OF CORRELATION AND REGRESSION ANALYSES, SIX SCAN STATIONS, 1967.

	Highest Correlation (in absolute value)	Best 3-variable subset	Standard Error of Estimate	Shrunken Multiple Correlation Coefficient*	Confidence Level
Anaheim	.30 (NO_2)	NO_2, mixing height, relative humidity	.11	.46	99.9%
Azusa	.59 (CO)	CO, mixing height, temperature	.10	.77	99.9%
Burbank	.48 (CO)	CO, mixing height, temperature	.11	.62	99.9%
Downtown Los Angeles	.30 (NO_2)	NO, NO_2, pressure	.10	.52	99.9%
La Habra	-.5 (mixing height)	Mixing height, relative humidity, sky cover	.019	.99	99.9%
Pasadena	-.59 (mixing height)	CO, mixing height, temperature	.092	.73	99.9%

* The shrunken multiple correlation coefficient reflects the reduction in correlation coefficient significance as a function of the degree of freedom which may be defined as the number of dependent variable observations minus the number of independent variables in the regression.

Table 6-5. RESULTS AUTO- AND CROSS-CORRELATION ANALYSES, SIX SCAN STATIONS, 1967.

	OX Autocorrelation lag 1	OX autocorrelation lag 2	Highest photochemical Cross correlation	Highest Meteorological Cross Correlation
Anaheim	.85	.61	-.47, NO at lag 0	.84, wind speed at lag 3
Azusa	.87	.68	-.51, NO_x at lag 1	.86, wind speed at lag 2
Burbank	.92	.76	-.52, NO at lag 5	.88, temperature at lag 1
Downtown Los Angeles	.87	.64	-.40, NO at lag 1	.5, wind direction at lag 3
La Habra	.85	.60	-.66, CO at lag 3	.85, temperature at lag 1
Pasadena	.88	.66	-.43, total HC at lag 3	.79, temperature at lag 2

three stations (Azusa, Burbank and Pasadena) having the highest frequency of high oxidant levels. For Azusa the shrunken multiple correlation coefficient was 0.77, indicating that these three variables could account for about 60 percent of the variability in maximum oxidant for that station. For La Habra, a different set of three variables accounted almost completely for the observed variation, but this is probably an accidental result of the extreme paucity of data for that station.

Table 6-5 summarizes the main results of auto-correlation and cross-correlation analysis. Oxidant auto-correlations exhibit the behavior described above, ranging between 0.85 and 0.92 for lag 1 hour. No noteworthy consistencies appear in the cross-correlation results, except that the highest coefficients for oxidant against other contaminants are always negative, while those for oxidant against wind speed and temperature are positive. No explanation is known. However, in the case of high correlations of oxidant against wind speed (with lag) at Anaheim and Azusa, the two SCAN stations farthest from the center of Los Angeles traffic, it may be suggested that the daily arrival of the sea breeze at the station foreshadows the arrival of photochemical oxidants in polluted air transported from centers of more intense emission of the primary photochemical contaminants.

2. The CAMP Cities as a Set

The photochemical pollution potential of the CAMP cities appears to be rather similar if the statistical properties of peak instantaneous and hourly average values of total oxidant concentrations are taken as criteria. For all

CAMP cities high peak oxidant levels are most likely to occur during the summer months between the 9th and 15th hours. Yearly mean values for the hourly average total oxidant concentration range from a low of 2.57 pphm for Washington to a high of 3.44 for St. Louis. Standard deviations ranged from a low of 2.02 for Chicago and Denver to a high of 2.3 for Washington. All CAMP cities recorded a modal hourly average value of 2 pphm. Fewer than 10 percent of all hourly values in each city reached 7 pphm or more.

Regression analysis produced predictive formulas yielding, at the worse, between -37 percent and +58 percent relative error with 95 percent probability. Of the 8 or 9 independent variables available, which did not include mixing height, nitric oxide occurred in five of the six best subsets of three independent variables; carbon monoxide appeared in two, total hydrocarbons and non-methane hydrocarbons each in one. Again, temperature occurred in five of these best sets of three variables, wind speed in two, and sky cover in one. No single set of three variables was best for more than one station. No best subset yielded a higher shrunken multiple correlation coefficient than Denver (0.57), for which the regression accounted for about 30 percent of the variability in hourly oxidant values.

Auto-correlation analysis showed uniform high correlation between successive hourly total oxidant averages. Cross-correlation analysis showed a strong negative serial correlation between total oxidant and NO as expected. Table 6-6 and 6-7 summarize the findings.

Table 6-6. RESULTS OF CORRELATION AND REGRESSION ANALYSIS, SIX CAMP STATIONS, 1967.

	Highest Correlation (in absolute value)	Best 3-variable Subset	Standard Error-at-Estimate	Shrunken Multiple Correlation Coefficient	Confidence Level
Chicago	.39 (total HC)	NO, total HC, temperature	.088	.49	99.9%
Cincinnati	-.21 (relative humidity)	NO, wind speed, temperature	.10	.30	95%
Denver	-.31 (NO)	NO, methane-free HC, temperature	.096	.57	99.9%
Philadelphia	-.25 (NO_2)	NO_2, temperature, sky cover	.098	.29	95%
St. Louis	-.29 (wind speed)	CO, NO, wind speed	.062	.54	99%
Washington	.48 (CO)	CO, NO, temperature	.10	.51	99.9%

Table 6-7. RESULTS OF AUTO- AND CROSS-CORRELATIONS, SIX CAMP STATIONS, 1967.

	OX Auto-correlation lag 1	OX Auto-correlation lag 2	Highest Photochemical Cross-Correlation	Highest Meteorological Cross-Correlation
Chicago (6-2 to 6-5)	.90	.73	-	-
Cincinnati (7-27 to 8-1)	.88	.53	-.64, total HC at lag 0	-
Denver (8-22 to 8-26)	.80	.63	-.82, NO_2 at lag 1	.25, wind speed at lag 5
Philadelphia (6-23 to 6-25)	.93	.81	-.52, NO at lag 2	.05, wind speed at lag 3
(8-15 to 8-18)	.92	.77	-.56, NO at lag 2	.44, wind speed at lag 2
(8-26 to 8-30) (a)	.76	.61	-.63, NO at lag 0	.47, wind speed at lag 0
St. Louis (6-29 to 7-2)	.91	.76	.54, NO_2 at lag 5	-.25, wind speed at lag 0
Washington (7-26 to 7-28)	.93	.82	-.53, NO at lag 1	.17, wind speed at lag 2
(11-17 to 11-21) (a)	.85	.66	.26, CO at lag 0	.54, wind speed at lag 1
(11-25 to 11-27)	.86	.67	.95, CO at lag 0	-.61, wind speed at lag 1

(a) Refers to a low oxidant day selected for experimental control

3. Comparison of the SCAN Stations and CAMP Cities

Comparative information from simple statistics on oxidant hourly values for the SCAN and CAMP networks were given in Table 6-3.

The following inferences may be drawn by comparison of the results shown in the tables:

- In general, the oxidant highs at the SCAN stations are one to three times as large as the largest CAMP city oxidant high.
- The SCAN stations exhibit much larger interstation and intra-station data variability than the CAMP stations.
- Mixing height plays the role of the most frequently appearing variable in the "3-variable best fits" at the SCAN stations, while temperature plays the corresponding role at the CAMP stations, where mixing height was not available.
- The shrunken correlation coefficients corresponding to the 3-variable regressions are higher at the SCAN stations.
- Total oxidant auto-correlation functions are very similar for both networks.
- There are significant cross-correlations of total oxidant with other meteorological variables for both networks.
- Hourly average oxidant during selected episodes at some SCAN stations showed high positive cross-correlation with wind speed, whereas this was not true for the episodes investigated at CAMP stations. In the latter, cross-correlation with wind speed were mainly low or negative.

4. Additional Analysis Possible

The initial analyses that were planned were completed within the resources available for this purpose. In general these analyses do not constitute a full exploitation of the analytical potential inherent in the special data bases that were constructed. Further analysis, especially discriminant analysis, appears to be indicated, with emphasis on the SCAN data. In particular:

1. Frequency distributions for high oxidant days should be compared with those for low oxidant days, to determine where the significant differences in the variables occur.
2. Frequency distributions should be obtained by hour of the day, and the values of all variables of interest should be retrieved and studied.
3. Data on non-methane hydrocarbons for Los Angeles should be collecte and utilized in this study.
4. More hypothesis formulation and testing should be performed. In particular, the relationship among values of contaminants in the morning and values of oxidants during the day should be explored, as suggested in Chapter 5, Air Quality for Hydrocarbons, (OHEW, PHS, EHS, NAPCA, March, 1970).
5. The degree of agreement (cross-correlation) between stations in the same air quality region, and the degree of dependence or independence of the variables should be established.
6. The extent of the smog cloud should be established.

CHAPTER 7

DIGITAL SIMULATION OF PHOTOCHEMICAL POLLUTION

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A. INTRODUCTION

Air quality models are tools that can be used in decision-making, particularly in the areas of planning, implementation and evaluation of air pollution control programs. Because computer-based models can handle many parameters and data files and rapidly perform computations, they can be conveniently used to analyze and predict pollution trends and episodes, assess the effects of pollution damage and alternative control plans, explore contaminant, environmental and source interactions, and train students and workers in the mechanisms and control of the air pollution system.

Acceptance of models in actual decision-making will depend on the degree of confidence that can be placed in the validity and logic of the mechanisms employed and the amount and quality of data available to test and use the models. Model building, therefore, should be looked upon as an evolutionary process--one that grows with the normal processes of analysis, control and evaluation. In particular it should interact with and contribute to the design of data collection systems and the management and analysis of aerometric, source emission and other needed data.

Models will have practical utility to the degree they reflect important aspects of physical and chemical reality. This requirement is best satisfied by the dynamic simulation model in contrast to statistical (e.g., regression) or limited empirical (e.g., diffusion) models which are based on patterns and which resort to artificial expedients to fit parameters.

Most air quality models in current use may be characterized as diffusion models. These are based on an empirical relationship, the diffusion equation, which describes a pattern of contaminant concentrations in an atmosphere surrounding a point source of emissions. The pattern described by this equation is static, i.e., does not vary with time. The diffusion equation is intended to apply only to situations of constant emission rate, constant wind direction and constant wind speed, and it would require that these conditions remain constant for an adequate period prior to any test of applicability.

An air quality model for photochemical contaminants is less amenable to the diffusion model approach, since the diffusion equations contain no factors to represent the interaction of contaminants. Such interactions are in no way related to spatial position, wind velocity, or distances from emission points. The development of important photochemical secondary contaminants, such as ozone, normally requires that the period of residence of the primary emissions in the atmosphere be more than an hour, even in bright sunlight. Experience has shown that existing diffusion models are highly unreliable in predicting concentrations of even non-reacting contaminants at distances from their sources corresponding to an hour's air movement.

A fully scientific air quality model for photochemical contaminants would clearly require a mathematical framework related to the chemistry of the photochemical contaminants. It would be able to predict concentrations of a large number of primary and secondary contaminant species as a function of time at any point in the region of interest, and auxiliary computer programs could derive, from these detailed predictions, predicted values of any desired air quality indices. A reactive model may represent the more general case of air quality modeling since relatively non-reactive contaminants, such as carbon monoxide, SO_2 and particulates can also be followed in the system.

B. THE REACTIVE POLLUTION ENVIRONMENTAL SIMULATION MODEL (REM)

A simulation model embodying current state-of-the-art principles of photochemical smog has been developed for the National Air Pollution Control Administration by the System Development Corporation under Contract CPA 22-69-108. The environmental mechanisms employed reflect those described in Chapter 3, Atmospheric Physics and Meteorology and the kinetics of chemical reactions are derived from those reviewed in Chapter 4, Atmospheric Reactions.

The structure of the computer program is basically that of a detailed episode model for chemical kinetics, with subroutines for estimating the location of the air parcel trajectories and the associated values of ultraviolet irradiance, mixing height, input of emissions from vehicular traffic and diffusion of contaminants from stationary sources*. The geometric setting is a standard two-dimensional urban grid system. Coded in Fortran IV for IBM Systems 360/50 and 67, a control program outputs parcel positions and pollutant concentrations at previously specified instants in simulated time. A meteorological subroutine interpolates wind and other data from input values at weather stations to points along the trajectory. A traffic subroutine generates emissions as a function of location and time of day, based on generalized or specific assumptions about traffic density and emission factors. An ultraviolet irradiance subroutine computes the relative rate of photolysis of nitrogen dioxide as a function of time of day, and a diffusion subroutine estimates contributions from upwind stationary sources to the parcel being followed.

---

* A mathematical description of the model is contained in Appendix II.

The general architecture of the model is shown in Figure 7-1. The functional elements of the model may be summarized as follows:

1. The Control Program

The Control Program accepts input data (the conditions specified for a given simulation), controls the logical sequence and temporal flow of the simulation, and outputs desired information. The inputs and outputs currently include the following.

Input	Output
Desired trajectory start position and time.	Pollutant concentrations.
Wind speed and direction.	Mixing depth (along the trajectory).
Barometric pressure.	Emissions (along the trajectory), HC, NO.
Temperature.	Trajectory time and coordinate positions.
Cloud Cover.	Reaction Rates.
Relative humidity or dew point.	Rates of change of the pollutants.
Station or receptor point position and elevation.	
Solar zenith angle.	
Radiosonde curves or mixing height.	
List of chemical species and initial concentrations.	

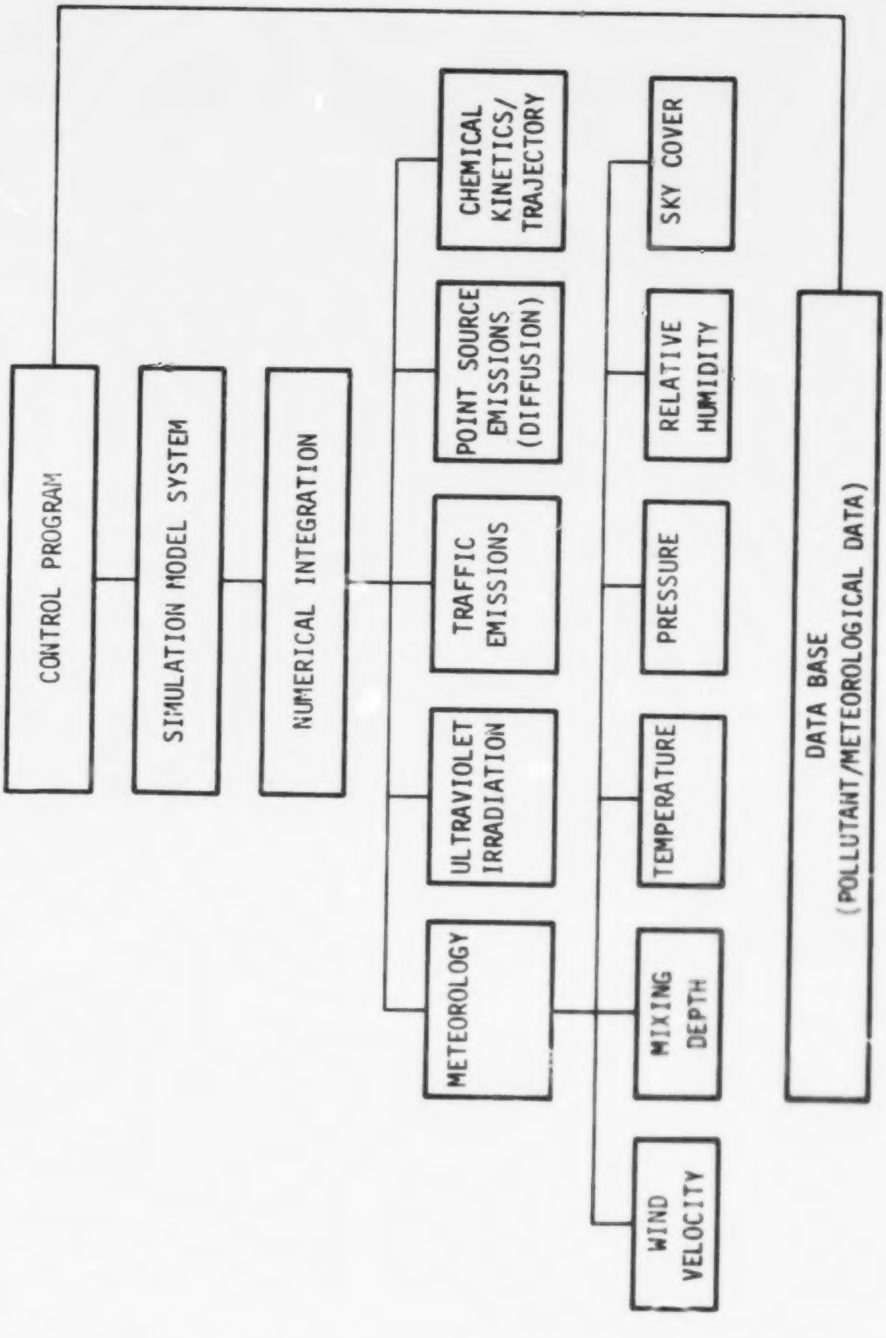

FIGURE 7-1 GENERAL MODEL ARCHITECTURE

Input (Continued)

Rate constants.

Traffic emissions (vehicle miles and distribution)

Stationary source data, stack height, diameter,
temperature, exit velocity, emission rate.

With minor program modifications, any of the input data can be standardized as "fixed" parameters, or parameters can be modified to reflect inputs which are desired to alter the design characteristics of the photochemical system. Thus the inputs can be made limited and simple or extensive and complex by presetting certain values within the code itself and reading in others at run time.

2. Meteorological Module

This consists of a series of subroutines which accepts actual wind velocity, temperature, pressure, humidity, cloud cover data, radiosonde and height above sea level for spatial interpolation to pollutant column position, estimation of mixing depth, and for calculation of time derivatives. Temperature and pressure inputs are required for the uv module, for estimations of horizontal diffusion, and for the source emission inputs in order to apply gas laws to estimating concentration-time derivatives in the column.

3. Ultraviolet Module

This subroutine calculates a diurnal uv function based on measurement of cloud cover, latitude and local calendar time. The module computes as a function of time and as a subset of the meteorological topographical variables the specific ultraviolet absorption rate of NO_2.

4. Transport Mechanism

This mechanism is an integral part of the Chemical Kinetics Module as described below. The transport of air parcels is determined by an interpolated trajectory based on actual wind direction and speed and other meteorological data derived from a "dense" network of meteorological stations. The present version operates from a data base of 22 wind stations. It has a capcity to handle 32 stations.

5. Source Emissions

The subroutine computes as a function of time the perturbative time rate contributions of NO, CO and propylene by application of emission factors to vehicle miles determined on the basis of grid distributed percentages of total vehicle miles, and diurnal mileage variations. The Los Angeles Basin is subdivided into a grid system of 784 equal 4-square-mile squares corresponding to a 56-mile by 56-mile square total area. The model also includes characterizing data for 12 large power plant sources. It has the capacity to accept other source emission input on demand. Stationary source emissions are computed by the Diffusion Module.

6. Diffusion Module

The model calculates mixing height and assumes instantaneous vertical mixing in the air parcel as a simplifying assumption. The trajectorized air parcel is geared to accept variable area source (grid) emissions, e.g., traffic emissions. Since stable conditions apply, lateral losses and gains from the air parcel are assumed to be equal. The model contains an optional horizontal diffusion subroutine for estimating downwind concentrations from large stationary sources, where stack height and other stack parameters are to be taken into account. This subroutine computes the perturbative time rate concentrations of pollutants from large upwind sources that contribute to the trajectory air parcel of interest.

7. Chemical Kinetics Module

This is a "reactor" mechanism, i.e., chemical reactions are taking place continuously within a moving parcel of air. This module has operated on 13-41 steps and is based on a sequence of stoichiometrically valid elementary reaction steps, previously validated against chamber data. The current version contains a 31-step mechanism (see Table 7-1). This mechanism preserves the flexibility of chemical detail necessary to relate to source emission species (primary contaminants) of interest on the one hand, and to permit following of the spatial and temporal distributions of secondary contaminant concentrations of interest on the other. The reaction steps, reaction rates and chemical species are easily modified and expanded on demand. Chemical mechanisms corresponding to different hypotheses can be input on short notice and integrated with the other environmental and meteorological mechanisms of the model.

This module computes the total time derivative of each of the photochemical pollutants (or reactants). This is accomplished by adding the perturbative derivatives input from the other modules to the corresponding right-hand side terms of a set of standard chemical kinetics ordinary differential equations. (The module also utilizes the wind velocity outputs from the Meteorological Module as the time derivatives of the position vectors that fit the air parcel trajectory.)

8. The Numerical Integration Module

On the basis of derivatives computed from the Kinetics Module, the Numerical Integration Module integrates all parcel pollutant concentrations and parcel positions forward in simulated time. This module is a standard numerical integration program based on Hamming's linear, multistep predictor-corrector method.

C. CURRENT STATUS AND DEVELOPMENT HISTORY OF THE MODEL

A prototype version of the model has been programmed and is in the validation and optimization phases. To arrive at this stage (1) each submodule was coded for operation and debugged under time-sharing; (2) a module-by-module maximum time-sharing usage approach was utilized to simultaneously maximize program development speed and minimize computer time costs; (3) only after each submodule was reviewed for computational correctness was the totality of modules linked, interfaced, and compiled together with the main control program.

The model is designed to be flexible and expandable. For example any reaction mechanism, chemical species of interest, reaction rates, traffic and stationary source information, and solar zenith angle diurnal curve is readily inserted. The first versions of the model delivered to NAPCA include the following optional features.

1. A 31-step reaction mechanism.
2. A mixing height determination routine (the model provides for both an A.M. and P.M. curve).
3. One solar zenith angle curve.

4. Areal traffic ratios based on 1960 data as obtained from Teague and on a diurnal traffic volume distribution curve. Los Angeles daily vehicle mileage for 1969 has been estimated at 120,000,000 miles from data supplied by the State of California.

5. Characterizing data for 12 stationary sources. These include exit velocity, height of stack, diameter of stack, height above sea level, temperature, and emission rate in pounds per hour, as obtained from local power plant sources.

D. MODEL VALIDATION

Preliminary validation runs of the model have been conducted through a series of simulations representing conditions in the Los Angeles Basin on September 30, 1969, a day on which elevated levels of oxidant were recorded at various monitoring stations in the Air Pollution Control District network. The trajectories generated by computer runs for this day are shown in Figure 7-2 and postulated rate constants in Table 7-1.

Input for these simulations consisted of weather data collected from 22 meteorological stations for September 30 and values of nitrogen dioxide, nitric oxide and ozone concentrations as observed at a chosen station at a chosen time of day on September 30. In addition, values for concentrations of hydrocarbons were arbitrarily assigned for the input, inasmuch as hydrocarbon readings were not available. For carbon monoxide a starting level of 5 ppm was assumed. Contributions of oxides of nitrogen from stationary sources were assumed negligible.

1. Thirty-One Step Mechanism

The mechanism incorporated in the kinetics module for these simulations was a set of 31 elementary (or quasi-elementary) steps, derived by simplification

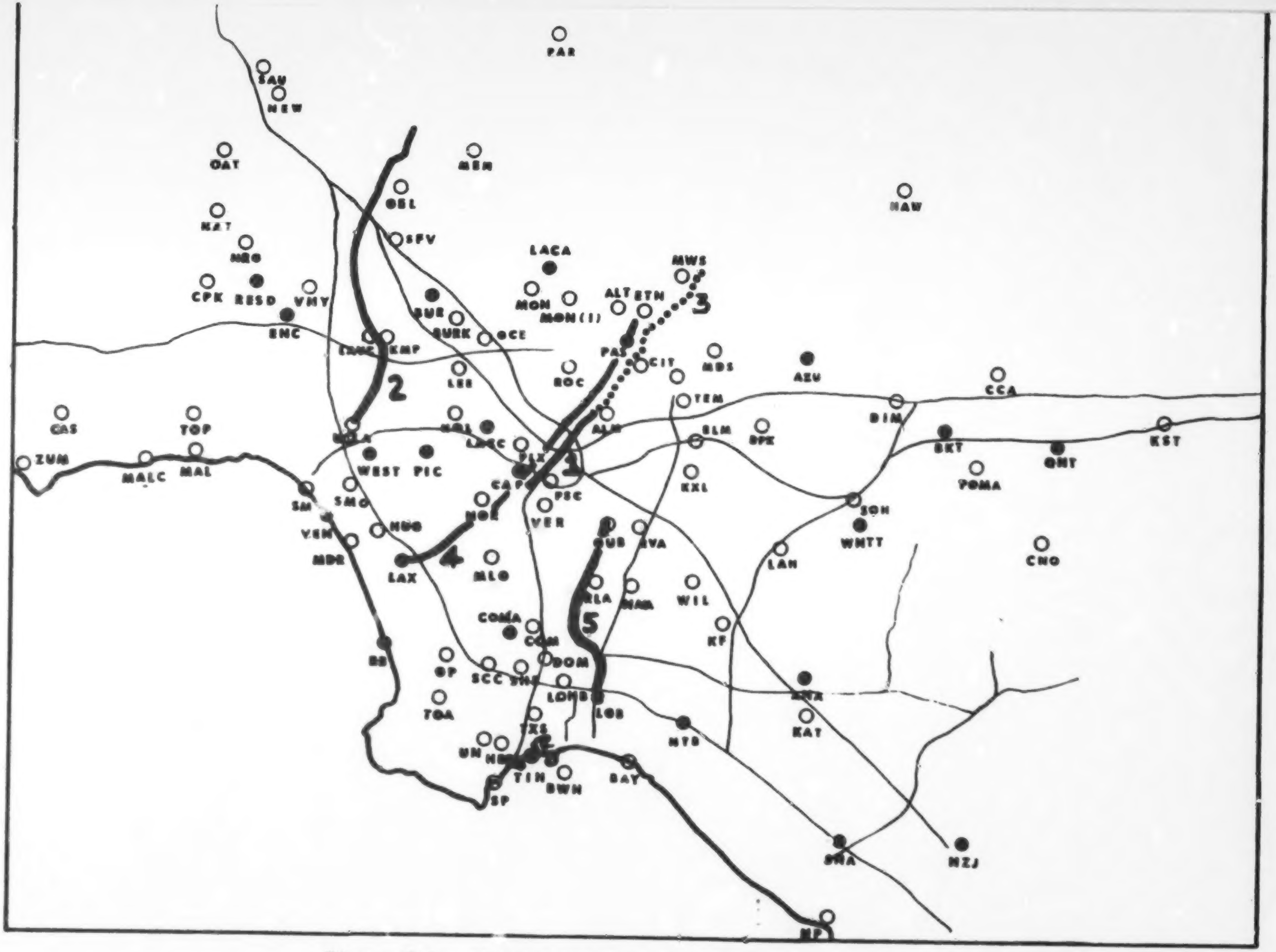

Figure 7-2. STATION LOCATIONS AND SIMULATION TRAJECTORIES.

```
0.6000E 02 MIN SIMULATION  RB=0.1200E 03  PRMT(3)=0.1000E-02  PRMT(4)=0.1000E-01
31 STEP MECHANISM                                                          SAMPLE23
NO = 1      C3H6 = 50
  22 METEOROLOGICAL STATIONS
  2 BARRIERS


K-VALUES FOR REACTIONS

   1      NO2+HV      =NO+O                0.10000000D 01      1  0  2 23  0
   2      O+O2+M      =O3+M                0.14000000D 07     23  0  3  0  0
   3      O3+NO       =NO2+O2              0.30000000D 00      3  2  1  0  0
   4      NO2+O3      =NO3+O2              0.10000000D-02      1  3 13  0  0
   5      NO3+NO2+H2O=2HNO3                0.85000000D 01     13  1  0  0  0
   6      NO3+NO      =2NO2                0.24500000D 03     13  2  1  1  0
   7      NO+OH       =NO2+H               0.10000000D 01      2 15  1 14  0
   8      NO+HO2      =NO2+OH              0.10000000D 02      2 16  1 15  0
   9      H+O2+M      =HO2+M               0.10000000D 07     14  0 16  0  0
  10      NO2+O       =NO+O2               0.50000000D 02      1 23  2  0  0
  11      NO+O+M      =NO2+M               0.10000000D 02      2 23  1  0  0
  12      NO2+OH      =HNO3                0.10000000D 04      1 15  5  0  0
  13      OH+O3       =HO2+O2              0.10000000D 03     15  3 16  0  0
  14      OH+CO       =H+CO2               0.30000000D 01     15  8 14  0  0
  15      CH3+O2+M    =CH3O2+M             0.14000000D 07     17  0 19  0  0
  16      CH3O2+NO    =CH3O+NO2            0.20000000D 02     19  2 18  1  0
  17      CH3O+O2+NO  =CH3O2+NO2           0.10000000D 02     18  2 19  1  0
  18      C2H3O+O2+NO=C2H3O2+NO2           0.10000000D 02     20  2 21  1  0
  19      C2H3O2+NO   =C2H3O+NO2           0.10000000D 03     21  2 20  1  0
  20      C2H4O2+NO   =CH3CHO+NO2          0.10000000D 03     22  2  6  1  0
  21      CH3O+O2     =HCHO+HO2            0.50000000D 01     18  0  7 16  0
  22      C3H6+O      =CH3+C2H3O           0.70000000D 03      4 23 17 20  0
  23      C3H6+O3     =HCHO+C2H4O2         0.10000000D-03      4  3  7 22  0
  24      C3H6+O+O2   =HCHO+C2H4O2         0.14000000D 03      4 23  7 22  0
  25      C3H6+OH+O2  =CH3O+C2H4O2         0.10000000D 02      4 15 19 22  0
  26      C3H6+HO2    =CH3O+CH3CHO         0.10000000D 01      4 16 18  6  0
  27      C3H6+CH3O2=CH3+CH3O+C2H3         0.10000000D 01      4 19 17 18 20
  28      C2H3O+M     =CH3+CO+M            0.50000000D 01     20  0 17  8  0
  29      CH3O+NO2    =CH3ONO2             0.10000000D 01     18  1  9  0  0
  30      C2H3O+O2+NO2=C2H3O3NO2           0.10000000D 01     20  1 10  0  0
  31      DUMHC+O     =CH3+C2H3O           0.70000000D 01     12 23 17 20  0
```

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Table 7-1. 31-STEP REACTION MECHANISM, REACTION RATES AND SPECIES NUMBERS.

of a 40-step mechanism previously validated in simulation of irradiation chamber experiments (see Chapter 4, Section F-4). Details of this mechanism (see Table 7-1) are as follows.

Of the 31 steps listed, the first three are the universally recognized set constituting the basic nitrogen dioxide photolysis cycle, discussed in Chapter 4, Section D-1. Reaction 4 is the well-recognized oxidation of nitrogen dioxide by ozone, which produces the standard form of nitrogen trioxide. Reaction 5 disposes of the nitrogen trioxide by formation of nitric acid vapor. (This is an example of the use of a pseudoelementary reaction to simplify the required computations: the rate listed is actually that of the bimolecular association of the trioxide with the dioxide to form N_2O_5, nitrogen pentoxide (or nitric anyhydride). It is assumed that nitric acid is formed rapidly, and that it is the only important product derived from the anhydride. This being the case, it is unnecessary to compute the concentration of nitric anhydride as an intermediate, and unnecessary to specify the concentration of water vapor.

Reactions 6 through 13 are inorganic reactions. All occur by bimolecular collisions except reactions 9 and 11, in which the presence of a third molecule is required for stabilization by removal of kinetic energy. (In such cases, the rate factor provided is a pseudoconstant, which incorporates the concentration of inert molecules as discussed in Chapter 4, Section F-3.)

Reaction 14 is provided to test whether the presence of relatively large concentrations of carbon monoxide could be expected to have detectable effects on the rate of consumption of reactants in the photo-oxidation system.

Reactions 15 through 30 provide for the consumption of hydrocarbons (typified by propylene) and their degradation to molecules of smaller carbon number through chains of free radical reactions. Reactions 17, 18, and 30 are postulated not to require trimolecular collisions; these are pseudoelementary steps in which it is assumed that a virtual equilibrium is established between a free radical and molecular oxygen as reactants and an oxygenated free radical intermediate. Reactions 24 and 25, on the other hand, might be considered to require essentially trimolecular collisions. Reaction 27 is a speculative chain branching step, incorporated for exploratory purposes.

Reaction 31 allows for effects of less reactive bydrocarbons. For the sake of simplicity, these hydrocarbons (labeled DUMHC) are assumed to have the same molecular formula as propylene, and to yield the same products as propylene on reaction with oxygen atoms. The rate constant of this reaction, however, is assumed substantially smaller than that for propylene.

Termination reactions between all free radical species present are also assumed to be part of the mechanism. Although these reactions are not explicitly included in the list of elementary steps, their effect is incorporated in the programming of the kinetics module. They are assumed to have a uniform rate constant of 1×10^3 $\mathrm{pphm}^{-1}\mathrm{min}^{-1}$. Products from these termination reactions, however, are not included among the products tabulated in the simulation.

2. Chemical Species Utilized

Species tabulated as reactants or products in the 31-step mechanism are listed in Table 7-2. Of these, the first four represent the components

Table 7-2

SPECIES INVOLVED IN 31-STEP MECHANISM

1.	NO_2	nitrogen dioxide
2.	NO	nitric oxide
3.	O_3	ozone
4.	C_3H_6	propylene (or reactive hydrocarbon)
5.	HNO_3	nitric acid vapor
6.	CH_3CHO	acetaldehyde
7.	HCHO	formaldehyde
8.	CO	carbon monoxide
9.	CH_3ONO_2	methyl nitrate
10.	$C_2H_3NO_5$	peroxyacetyl nitrate
11.	Fixed O_2	fixed oxygen parameter (see text)
12.	DUMHC	less reactive hydrocarbon
13.	NO_3	nitrogen trioxide
14.	H	hydrogen (free atom)
15.	OH	hydroxyl (free radical)
16.	HO_2	hydroperoxyl (free radical)
17.	CH_3	methyl (free radical)
18.	CH_3O	methoxyl (free radical)
19.	CH_3O_2	peroxymethyl (free radical)
20.	C_2H_3O	acetyl (free radical)
21.	$C_2H_3O_2$	peroxyacetyl (free radical)
22.	$C_2H_4O_2$	acetaldehyde oxide (or "zwitter ion")
23.	O	oxygen (free atom)

most often monitored in connection with photochemical smog, nitrogen dioxide, nitric oxide, ozone and hydrocarbons, respectively. Nitric acid (species 5) is suspected of being a major product in the photo-oxidation, but is almost never quantitatively measured in the atmosphere. Aldehydes, represented by acetaldehyde (species 6) and formaldehyde (species 7), are known to be formed, but quantitative information on atmospheric levels is scarce. Methyl nitrate (species 9) and peroxyacetyl nitrate (species 10) are assumed to be the principal organic nitrogen-containing products.

"Fixed 0_2", listed as species 11, is not a real chemical species but a chemical parameter included here for convenience. It represents the amount of molecular oxygen incorporated into products of the reaction complex; as such it is not readily subject to experimental validation. Molecular oxygen produced in steps 3, 4, 10 and 13 is registered negatively in this parameter, which may therefore legitimately acquire negative values under some circumstances.

Species 12, "DUMHC," is provided as a less reactive hydrocarbon, participating only in Reaction 31. Species 13 through 23 are all intermediate compounds, assumed not to accumulate to appreciable concentrations. Species 13 through 21 are all odd-electron species. Nitrogen trioxide (species 13) is the first product of oxidation of nitrogen dioxide by ozone, but reacts very rapidly with either nitrogen dioxide or nitric oxide. Hydrogen atoms (species 14) and seven free radicals (species 15 through 21) also fall in the odd-electron category. The remaining intermediate species utilized in this mechanism are a hypothetical acetaldehyde-oxide or zwitter ion (species 22), and the free oxygen atom (species 23).

3. Trajectory Simulation

Initial conditions imposed in the various simulations are indicated in Table 7-3 and calculated vs. observed values at terminal points for five trajectory runs are shown in Table 7-4. In the first run, the starting location and time were set to downtown Los Angeles at 1:00 P.M., and a simulation time of one hour was specified. The trajectory generated in the simulation moved toward the northeast, for a total distance of about six miles; computer running time was about 4 minutes, for a ratio of simulation time to run time of about 16 to 1.

The second run computed a trajectory of nearly 5 hours, starting in West Los Angeles at 10:00 A.M. This showed the original air parcel moving almost due north across the Santa Monica mountains and eventually arriving in the San Fernando Valley. Run time was nearly 40 minutes in this case, for a ratio of simulation time to running time about 8 to 1.

A third run was undertaken, using the same starting location and time as the first run, but allowing for three hours of simulated time lapse rather than one, to enable the trajectory to develop closer to the air monitoring station in Pasadena, thus generating simulated contaminant concentrations which could be reasonably compared with observations from that station. This run yielded a simulation time ratio of sixteen to one, in agreement with run one.

A fourth run was computed, starting at the Los Angeles International Airport at 11:00 A.M., and terminating after four hours at Pasadena. This

Table 7-3. INITIAL CONDITIONS FOR SIMULATIONS.

	Simulation				
	No. 1	No. 2	No. 3	No. 4	No. 5
Starting Point	DOLA	WLA	DOLA	LAX	LB
Starting Time	1300	1200	1300	1100	0800
Initial NO_2, pphm	13	14	8	18	22
Initial NO	1	1	5	7	38
Initial O_3	15	9	17	2	1
Initial C_3H_6	50	50	50	50	50
Initial DUMHC	50	50	50	50	50
Rate constant, step 13	100	100	20	20	20
Rate constant, step 21	10	10	5	5	5
Rate constant, step 22	140	140	70	70	70
Rate constant, step 25	10	10	1	1	1
Rate constant, step 27	10	10	1	1	1
Rate constant, step 28	10	10	5	5	5
Rate constant, step 29	10	10	1	1	1
Rate constant, step 30	10	10	1	1	1

Table 7-4

PHOTOCHEMICAL MODEL CALCULATED VERSUS OBSERVED AIR POLLUTANT CONCENTRATIONS

INTERMEDIATE AND TERMINAL TRAJECTORY POINTS
PREDICTED VALUES*VERSUS OBSERVED-NEAREST STATION (PPHM)

MODEL VERSION	RUN NUMBER	STARTING LOCATION	STARTING TIME	TERMINAL LOCATION	TERMINAL TIME	03 COMP/ OBSER.	NO COMP/ OBSER.	NO_2 COMP/ OBSER.	HC COMP/ OBSE
AA	1	Downtown Los Angeles	1300	Downtown Los Angeles	1400	5/13	0/4	1/8	12/**
AA	2	UCLA	1000	Reseda	1500	16/5	0/1	1/1	1/*
AA	3	Downtown Los Angeles	1300	Pasadena	1500	12/15	1/1	10/5	32/**
*** AB	4	Lennox	1100	Downtown Los Angeles	1300	12/17	1/5	14/8	53/**
				Pasadena	1500	21/15	0/1	1/5	42/**
AB	5	Long Beach	0800	Downtown Los Angeles	1200	12/15	1/6	14/8	56/**

* Computed values are instantaneous calculations, observed values are hourly averages.

** No recorded data.

*** Version AB includes optimized numerical integration procedure, and other improvements.

trajectory showed the parcel moving towards downtown Los Angeles and paralleling run three to Pasadena. The ratio of simulation time to running time was about fourteen to one.

Finally, a run on a starting location in Long Beach at 8:00 A.M. yielded a much smaller simulation time ratio, near unity, with relatively short travel distance toward the north. This timing anomaly may be explained by the large magnitude of traffic pertubation derivatives induced by small computed mixing heights. Indeed, it has been subsequently observed that the smaller these traffic pertubations, the greater is the simulation time ratio.

Contaminant concentrations calculated from the simulations are shown as functions of simulated elapsed time in Figures 7-3 and 7-4. Values for nitrogen dioxide, propylene and ozone for runs 1 and 3 appear in Figure 7-3. The obvious differences in simulated behavior of the contaminants in these two runs result mainly from changes in selection of rate constants for certain elementary steps. These changes, indicated in Table 7-3, were intended to reduce the expected rates of consumption of the primary reactants, as those rates seemed substantially too high in runs 1 and 2. With the new choices, the values predicted for ozone, nitrogen dioxide and nitric oxide were all within 5 pphm of the observed values at the Pasadena air monitoring station at the time of closest approach of the trajectory to that station. These validating points are also shown in Figure 7-3. (Validation data for the hydrocarbon concentration are not available.)

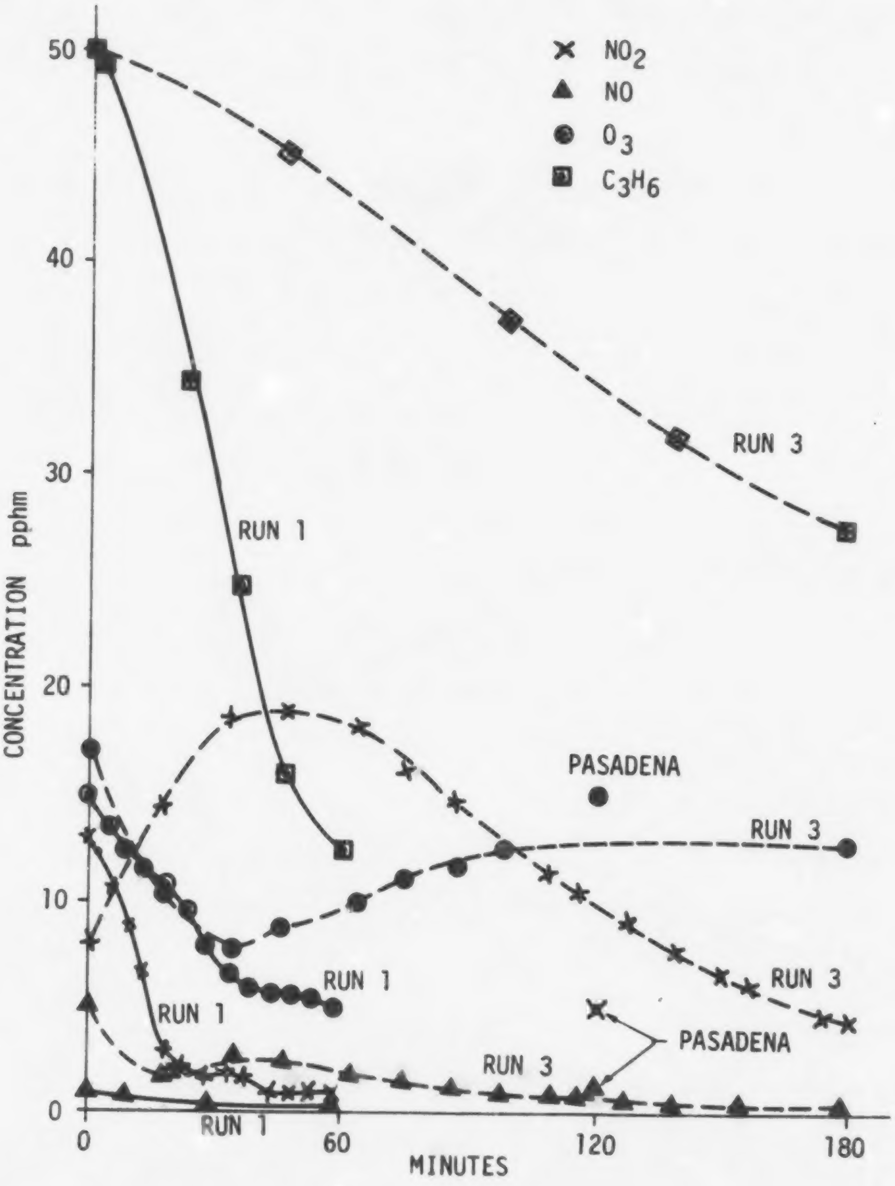

Figure 7-3. CONTAMINANT CONCENTRATIONS VS SIMULATED TIME LAPSE, RUNS 1 AND 3.

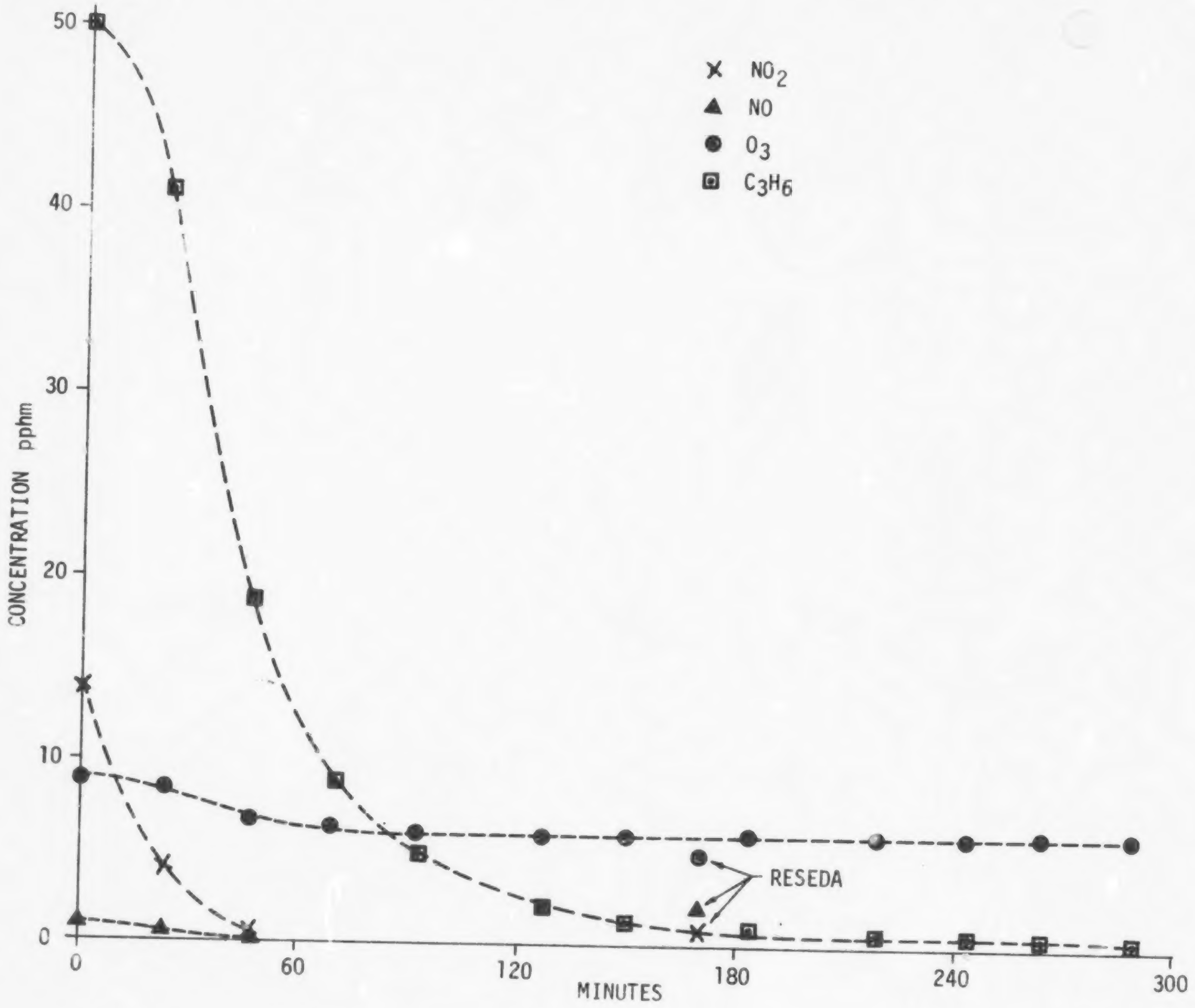

Figure 7-4. CONTAMINANT CONCENTRATION VS SIMULATED LAPSE TIME, RUN 2.

E. APPLICATION OF THE MODEL

After optimum operation and adequate validation and sensitivity analyses have been achieved, the model will be useful in many ways for application to practical problems in the control of air quality. Thus, for regions where weather variables and air quality are well documented, the model will predict the effect on air quality of postulated trends in emissions rates, either uniform or geographically biased. With air quality models based on standard types of diffusion equations, typical contaminant concentrations tend to increase proportionally to increases in emission rates. However, with the secondary contaminants generated as a result of photochemical reactions in the atmosphere, no such relation holds, nor is any simple relation adequate for describing the changes effected.

Similarly, an adequately validated model will predict the air quality effects of proposed new stationary sources of oxides of nitrogen or hydrocarbons.

For regions without air monitoring data, but with good information about weather and emissions, the model can be used to produce detailed estimates of air quality. For regions with only a single air monitoring station, or with an inadequate number of stations, the model will provide estimates of the variation of air quality with location within the region.

Even if no detailed information regarding emissions and weather exists for the region of interest, potentials for serious photochemical air pollution can be projected from various reasonable assumptions which can be readily tested by application of the computer model.

A preliminary study of the application of the model to a control strategy exercise was conducted. In this study the existing weather for September 30, 1969, total vehicle mileage and distribution of vehicle mileage were maintained, but the emission rates for hydrocarbons (propylene) and NO were modified by 6 sets of relative factors, as follows:

RUN	1	2	3	4	5	6
NO	1	1	.5	.5	.1	.1
HC	.25	.05	.25	.05	.25	.05

Each set represents a conceivable control strategy test. The objective of the tests is to determine which combination of emission factor reductions (HC and NO) best minimize contaminant concentrations, particularly ozone. Results of these runs are presented in Table 7-5 in terms of calculated concentrations of the contaminants (nitrogen dioxide, nitric oxide, ozone and hydrocarbons) at the terminus of the trajectory, near Pasadena, and in terms of the maximum calculated concentrations of the contaminants (which may be found at other points of the trajectory.) Also listed is the "fixed oxygen", a measure of the cumulative degree of reaction at the end of the trajectory.

From Table 7-4 it will be noted that hourly average concentrations observed in Pasadena for 1500 to 1600, the hour of the trajectory approach, were 5 pphm NO_2, 1 pphm NO, and 15 pphm oxidant, with no reading on hydrocarbons.

Table 7-5

Calculated Photochemical Contaminant Concentrations for Lennox-Pasadena Trajectory, with Varied Emissions Input

Run Number		0[a]	1	2	3	4	5	6
Initial NO, pphm		7	8	8	4	4	0.8	0.8
Initial HC, pphm[c]		50	12.5	2.5	12.5	2.5	12.5	2.5
Input NO, relative[d]		1	1	1	0.5	0.5	0.1	0.1
Input HC, relative[d]		1	0.25	0.05	0.25	0.05	0.25	0.05
NO_2, pphm:	Pasadena	1	38	39	20	26	6	14
	maximum	21	46	39	28	26	(18)[b]	(18)[b]
NO, pphm:	Pasadena	0	5	18	2	10	1	3
	maximum	7	19	37	7	18	3	5
O_3, pphm:	Pasadena	21	7	2	9	2	11	4
	maximum	21	7	3	9	4	11	5
HC, pphm:	Pasadena	42	18	4	18	4	17	4
	maximum	81	27	6	28	5	26	6
Fixed oxygen, pphm		155	45	15	37	10	34	7

a. Run 0 is the reference run, Table 7-4.

b. Maxima of 18 pphm NO_2 occurred at the starting point of the trajectory because the assumed initial value was 18.

c. "HC" is assumed as propylene in the mechanism used.

d. Factors applied to emissions input in the reference run.

For the reference run, the corresponding calculated values were 1 pphm NO_2, zero NO, and 21 pphm ozone. From the results in Table 7-5, it is clear that computed values of NO_2 for Pasadena are drastically increased by reducing the assumed hydrocarbon input without altering the oxides of nitrogen inputs (cf. Runs 1 and 2), while simultaneously the calculated values for NO are increased, and those for ozone and hydrocarbons strongly reduced. At lower input levels of nitric oxide, the same trends are evident (Runs 4 vs 3, and 6 vs 5), although not to as great an extent. Only in Run 5, with NO input one-tenth and hydrocarbon one fourth of that in the reference run, do the calculated values of NO_2, NO and oxidant in Pasadena approach the observed values: NO_2 6/5, NO 1/1, Ox 11/15. (pphm observed/pphm calculated).

Comparison of the calculated contaminant levels for Pasadena with the calculated maximum contaminant levels shows that the calculated ozone level at the Pasadena terminus was at the maximum for all runs with hydrocarbon input 0.25 of that in the reference run, but was less than the maximum for those runs with hydrocarbon 0.1. On the other hand, calculated NO_2 maxima occurred at the Pasadena terminus only for runs 2 and 4, with hydrocarbon input 0.1. Thus the model, with its assumed chemical mechanism, predicts that hydrocarbon control in the Los Angeles Region would have opposite effects on ozone and oxides of nitrogen as measured in Pasadena, at least for conditions like those of September 30, 1969.

Further exploration of the implications of these results may be facilitated by the presentation given in Table 7-6. Here the contaminant levels

Table 7-6

Calculated Contaminant Levels from Simulation Runs with Modified Emissions Input, Arranged for Easy Comparison

Pattern (Run No.):		Relative HC Input		
		1.00	0.25	0.05
Relative	1.0	0[a]	1	2
NO	0.5		3	4
Input	0.1		5	6

Nitrogen Dioxide, pphm

at Pasadena			Trajectory maximum		
1	38	39	21	46	39
	20	26		28	26
	6	14		(18)	(18)[b]

Nitric Oxide, pphm

at Pasadena			Trajectory maximum		
0	5	18	7	19	37
	2	10		7	18
	1	3		3	5

Ozone, pphm

at Pasadena			Trajectory maximum		
21	7	2	21	7	3
	9	2		9	4
	11	4		11	5

Table 7-6 (Continued)

Hydrocarbons, pphm					
at Pasadena			Trajectory maximum		
42	18	4	81	27	6
	18	4		28	5
	17	4		26	6

a. Run 0 is the reference run (Table 7-3)

b. Maxima of 18 pphm NO_2 occurred at the beginning of the trajectory because of constant assumed initial value.

taken from Table 7-4 and 7-5 are arranged in a pattern such that, for each contaminant, the values predicted on reducing hydrocarbons at constant NO input are entered across rows, the the values predicted on reducing NO at constant hydrocarbon input are entered down columns. Within the range tested, the principal implications of the model with the assumed chemical reaction mechanism appear to be the following:

1. Decreasing hydrocarbon input should cause decreases in ozone and hydrocarbon levels at Pasadena, with increases in nitric oxide and nitrogen dioxide levels.

2. As to the maximum contaminant levels at points between Lennox and Pasadena, decreasing hydrocarbon input should cause first an increase, then a decrease for nitrogen dioxide. For the other contaminants, the maximum levels would behave in generally the same way as the Pasadena levels.

3. Decreasing nitric oxide input should cause decreases in nitric oxide and nitrogen dioxide levels at Pasadena, but an increase in ozone levels. Hydrocarbon levels would be little affected.

4. Decreasing nitric oxide input should have effects on maximum contaminant levels similar to those described for Pasadena levels.

The application of the Reactive Pollution Simulation model requires an orientation to the modeling of air pollution that differs considerably from the diffusion model approach. The latter provides for a capability to deal with multiple point, line or area sources, multiple receptor points, and to display averages of pollutant concentrations on a grid system which represent seasonal or annual time periods of interest.

The diffusion approach lends itself to a gross picture of relative pollution levels over a geographic region of interest. It has the advantage of displaying values simultaneously. It has the disadvantage of poor accuracy, of not being able to dynamically simulate meteorological conditions, reactive contaminants or episode conditions.

The Reactive Model, on the other hand, is an episode model and simulates conditions as they occur on a diurnal basis and outputs "instantaneous" concentrations along a calculated air parcel trajectory.

In general the differences in the two approaches can be seen in terms of isopleth construction (lines of equal concentration of a single contaminant), and trajectory plots which output many contaminant concentrations for an unlimited number of receptor points along the trajectory. The contaminant concentrations are governed by time and position and therefore are not simultaneous. The values output are "quasi-instantaneous" in character, i.e., the rates of change of the concentrations of contaminants are comparatively small over any 5-minute interval. Thus model calculated values can be reasonably compared with 5-minute average observations. For validation purposes, these can be considered to fall with the range of observed hourly value observations.

Given these characteristics, the use of this model for analysis of seasonal, annual and other long term conditions based on the distribution of receptor points throughout the air quality region of interest requires the following approach:

1. Multiple Receptor Points - The determination of air quality at multiple receptor points (other than those output along a single trajectory) requires the use of a backward trajectory plotting technique. Points are selected by coordinate position and time. A backward trajectory is plotted to determine the trajectory start point. The trajectory is then run forward with kinetics routine to establish the air quality at the desired receptor point. Air quality at an unlimited number of receptor points can be so calculated. The data generated can be used as a basis for isopleth plotting.

2. Representative Air Quality - The depiction of representative conditions (monthly, seasonal, annual time periods) must be arrived at through characterization of meteorological conditions which represent days which are typical of the time periods of interest for the given air quality region under study. This requires that meteorological data of the given region be statistically characterized particularly in terms of wind speed, direction, mixing height and other meteorological and environmental parameters of interest. These can be grouped into days which are conducive to acute, moderate and light episode potentials. Meteorological data describing these representative days can be input to the model.

3. Artificial Trajectories and Multiple Trajectories - Where complete knowledge of the wind regime of a region is available, trajectories can be artificially plotted from streamline or other summary data and corresponding wind data can be assigned to the coordinate points. This technique has the advantage of hypothesizing and testing meteorological conditions which maximize the build-up of contaminants to produce acute episodes. Also this

technique provides the capability of standardizing sets of representative meteorological conditions for mass-testing many urban regions for their reactive pollution potentials, and for testing a variety of urban-source-configurations and emission rates.

4. Non-Photochemical Contaminants - The model readily handles non-reactive contaminants--CO, SO_2, particulates. The model can operate either with all contaminants simultaneously--photochemical and non-photochemical--or the chemical kinetics mechanism can be suppressed in order to operate with only non-reactive contaminants.

APPENDIX I

RESULTS OF STATISTICAL ANALYSIS

I. INDIVIDUAL LOS ANGELES SCAN STATIONS

A. ANAHEIM

1. Rank Order Analysis

The peak instantaneous value of 43 pphm for total oxidant concentration was recorded on August 28, 1967 during the 13th hour. On 113 occasions the daily instantaneous peak reached a value of 14 pphm or greater. The 14th is the modal hour of occurrence of peak oxidant concentration with 27 out of 113 such events taking place in that hour. Fighty-five percent of all peak instantaneous values occur between the 11th and 14th hour. October is the modal month of peak instantaneous oxidant levels with 20 events out of a total of 113. During the 9th hour on August 28, 1967 a peak instantaneous value of 17 pphm of NO_2 was recorded. This is the 12th highest reading in the NO_2 instantaneous daily peak population.

2. Frequency Distribution and Sample Statistics

The frequency distribution of hourly average oxidant concentrations is strongly skewed to the left with a mean of 3.45 pphm, a standard deviation of 3.93 pphm and a mode of 1 pphm. More than 96 percent of the hourly average oxidant concentration readings fall below 14 pphm. The value 14 pphm is 2.68 sample standard deviations from the mean.

3. Correlation and Regression Analysis

The largest correlation of .30 among dependent and independent variables was found to be between the total oxidant concentration logarithmic variable and the NO_2 logarithmic variable. The next correlation (in absolute value) of -.28 was for mixing height. In a 7-variable regression (CO, NO_2, mixing height, wind speed, temperature, relative humidity and sky cover) a standard error of estimate of .102 and a shrunken correlation coefficient of .55 were attained at the 99.9-percent level of confidence. From the above standard error of estimate the following 95 percent relative error confidence interval was computed:

$$.63(OX_M) \leq (OX_R) \leq 1.6\ (OX_M)$$

4. Auto and Cross-Correlation Analysis (August 26 to August 30)

As with the CAMP cities it can be seen that during a string of high oxidant days total oxidant is highly sequentially correlated. CO and NO_2 and NO and total hydrocarbons auto-correlation functions are, in general, quite similar. Meteorological variable auto-correlation functions are included for comparison. In the cross-correlation analysis the highest cross-correlation calculated between oxidant and other photochemical contaminants was -.47 at lag 0 for NO. Among the meteorological variables, there was a cross-correlation of .84 at a lag of 3 hours for total oxidant concentration versus wind speed. This result seems to be clearly indicative of a wind-transport phenomenon. Total oxidant was well cross correlated positively (.78 at lag 1) with temperature and fairly cross correlated with mixing height negatively (-.45 at lag 1).

B. AZUSA

1. Rank Order Analysis

The peak instantaneous observed concentration of 73 pphm was recorded on August 30, 1967 during the 12th hour. On 204 days a peak instantaneous value of 14 pphm or greater was recorded. The 14th hour is the modal peak oxidant hour with 57 out of 204 peaks taking place in that hour. 87.5 percent of all peaks are attained between the 12th and 15th hours. August is the modal month of peak oxidant level occurrence with 34 incidents out of 204.

On the highest peak oxidant day of the year the peak instantaneous NO_2 reached its 15th highest recorded value of 15 pphm during the 8th hour.

2. Frequency Distribution and Sample Statistics

The frequency distribution for average hourly oxidant concentrations is left skewed with sample mean of 5.4 pphm, standard deviation of 7.12 pphm and modal value of 1.00 pphm, with 2833 out of total population of 8040 readings recorded at this level. The value 14 pphm exceeds 89.99 percent of population values and is 1.23 standard deviations from the mean.

3. Correlation and Regression Analysis

In a sample of 204 points the lag of the maximum total oxidant concentration had the highest correlation of .6 with the 3-hour logarithmic average of CO concentration. This was followed by correlation of -.55 and .54 with mixing height and temperature. A 7-variable subset (CO, mixing height, wind speed, pressure, temperature, relative humidity and total sky cover) yielded a regression significant at the 99 percent level of confidence, with a standard error of estimate of .092 and a shrunken multiple correlation coefficient of .81. The standard error of estimate gives as the corresponding 95-percent confidence relative error band:

$$.65(OX_M) \leq (OX_R) \leq 1.53(OX_M)$$

4. Auto- and Cross-Correlation Analysis (August 26 to August 30)

Characteristically, during episodic lag sequences total oxidant is very highly sequentially correlated. The corresponding auto-correlation function takes on values of .87, .65, .42, etc., through lags 1, 2, and 3. In this particular case it is noted that the mixing height auto-correlation function is similar to that of total oxidant. Generally, most pollutant and meteorological auto-correlation functions indicate a temporal persistence. The exceptions here are CO, NO, and NO_2. In the cross-correlation analysis a very high cross-correlation of .86 between total oxidant concentration and wind speed is exhibited at a lag of 2 hours, with significant cross-correlation values down to a lag of 5 hours. This result is a very strong indication of the existence of a wind transport phenomenon.

C. BURBANK

1. Rank Order Analysis

The peak instantaneous oxidant concentration of 51 pphm was attained on July 21, 1967 during the 12th hour. On 182 occasions the peak instantaneous recorded concentration equaled or exceeded 14 pphm. The modal hour of peak oxidant occurrence is the 12th hour, with 61 out of 182 peak oxidant incidences in that hour. Ninety percent of all peaks are observed between hours 11 and 14 inclusive. July and August are the modal months of peak oxidant cocurrence, being together responsible for 72 out of 182 such episodes. On July 21, 1967 the 9th highest instantaneous peak level of 42 pphm of NO_2 concentration was recorded during the 8th hour.

2. Frequency Distribution and Sample Statistics

The frequency distribution of 7992 hourly average total oxidant concentrations is skewed to the left with mean of 4.64 pphm, standard deviation of 6.17 pphm and mode of 1.00 pphm. Ninety percent of all observed concentrations are exceeded by 14 pphm. The value 14 pphm is 1.52 sample standard deviations from the sample mean.

3. Correlation and Regression Analysis

The total oxidant logarithmic variable was most highly correlated with the CO logarithmic average with corresponding correlation coefficient of .48, with the logarithmic temperature correlation at .47, and the logarithmic mixing height at -.40. A 3-variable subset (CO, mixing height, and temperature) gave regression results significant at the 99 percent level (99.999.....9 percent) with a corresponding standard error of estimate of .11 and a shrunken multiple correlation coefficient of .62. The above standard error of estimate produces the following 95-percent confidence band for the oxidant concentration, (OX_R), predicted from the regression equation.

$$.6(OX_M) \leq (OX_R) \leq 1.66(OX_M)$$

4. Auto- and Cross-Correlation Analysis, (July 18 to July 22)

All contaminant (CO, NO, NO_2, NO_x, and total oxidant) auto-correlation functions exhibited the persistence phenomena previously described for Azusa. Total oxidant auto-correlation had the highest lag 1 value at .93, while total oxides of nitrogen had persistently high auto-correlations ranging from .90 at lag 1 down to .51 at lag 4. The highest cross-correlation of total oxidant with another photochemical pollutant was -.52 at lag 5 with NO. Cross-correlations of total oxidant with the meteorological variables was characterized by a cross-correlation of .88 for temperature at a 1-hour lag and .74 for wind speed at a 4-hour lag--again indicative of wind transport.

D. DOWNTOWN LOS ANGELES

1. Rank Order Analysis

The peak instantaneous oxidant concentration of 45 pphm was recorded on October 18, 1967 in the 13th hour. On 144 days peak levels of 14 pphm or more were attained. The 11th hour is the modal episode hour with 39 out of 144 such events occurring in the interval between 11:00 A.M. and 12 noon. Ninety-two percent of all peak oxidant events take place between the hours of 11 and 14, inclusive. August is the modal month of high oxidant events, with 27 out of 144. On October 18, 1967 during the 23rd hour a peak instantaneous concentration of 41 pphm of NO_2 was recorded. This was the 11th highest peak instantaneous value.

2. Frequency Distribution and Sample Statistics

The total hourly average oxidant concentration population of 8202 observations has the characteristic left skewedness with sample mean 3.34 pphm, standard deviation 4.15 pphm and modal value of 1.00 pphm. Ninety-six percent of the population values are exceeded by 14 pphm. This latter value is 2.57 sample standard deviations from the mean.

3. Correlation and Regression Analysis

The highest correlation in a sample of 144 between dependent and independent variables was .30 for the 3-hour logarithmic average of NO_2. A 6-variable subset (CO, NO, NO_2, pressure, relative humidity and sky cover) yielded significant regression results with corresponding standard error of estimate at .098 and shrunken multiple correlation coefficient of .55. From the above standard error of estimate is computed the following 95 percent confidence interval:

$$.64(OX_M) \leq (OX_R) \leq 1.57(OX_M)$$

4. Auto- and Cross-Correlation Analysis, (October 10 to October 20)

The auto-correlation functions for NO_2 and total hydrocarbons followed by total oxidant represented the strongest "persistence" phenomena. Again total oxidant was the most strongly serially correlated time series with an auto-correlation value of .87 at lag 1, 64 at lag 2, etc.

There was no striking cross-correlation between total oxidant and either the other photochemical contaminants or meteorological variables; -.41 with NO concentration at a lag of 2 hours, -.46 with mixing height at lag 0 and .5 wind deviation at lag 3. There was no significant indication of transport, the wind speed cross-correlation taking on a maximum value of .2 at lag 0.

E. LA HABRA

1. Rank Order Analysis

The peak instantaneous concentration of 31 pphm was recorded on October 11, 1967 during the 14th hour. On 54 recorded occasions a peak instantaneous total oxidant concentration of 14 pphm or more was reached. The 13th hour is the modal oxidant episode hour, with 13 out of 54 occurrences of high oxidant levels ($\geq$ 14 pphm) recorded in that hour. Forty-eight out of 54 high oxidant events occurred from the 12th to the 15th hours, inclusive. October is the modal month of high oxidant. The 6th largest peak instantaneous NO_2 concentration of 24 pphm was observed during the 16th hour on October 11, 1967.

2. Frequency Distribution and Sample Statistics

The sample population of 1350 total oxidant concentration was left skewed with mean 2.84 pphm standard deviation 3.95 pphm and mode 0.00 pphm. Over 97 percent of the population values were less than 14 pphm. The value 14 pphm lies 2.82 standard deviations from the mean.

3. Correlation and Regression Analysis

In a small sample size of 20, limited by missing data, the highest correlation (in absolute value) between dependent variable and independent variables was -.5 for the 3-hour logarithmic average of mixing height. The correlation with the 3-hour logarithmic average of sky cover was .3. A 3-variable regression (mixing height, relative humidity, sky cover) gave results significant to the 10th decimal place with standard error of estimate .019 and shrunken multiple correlation coefficient .99. The 95 percent confidence interval for the regression formula predicting total oxidant (OX_R) is given by:

$$.96(OX_M) \leq (OX_R) \leq 1.04\ (OX_M),$$

where it is recalled that (OX_M) is the observed value of total oxidant concentration. These results are of little importance because of the small sample size.

In the auto- and cross-correlation analysis results similar to those previosuly discussed for SCAN stations are generally obtained: high serial correlation of total oxidant and other contaminant concentration, fairly high cross-correlation of oxidant concentration with wind speed indicative of transport, etc. There is a high cross-correlation of .85 at a lag of 1 hour for temperature. There is a fairly high temporally persistent cross-correlation for sky cover. Since the number of samples in the cross-correlation analysis is about six times greater, higher confidence may be placed in the results of the auto- and cross-correlations, than in those for correlation and regression.

F. PASADENA

1. Rank Order Analysis

The peak instantaneous concentration of 53 pphm of total oxidant was recorded on August 29, 1967. On 189 occasions daily peak values equaled or exceeded 14 pphm. The modal hour of peak instantaneous total oxidant concentration was 13, with 52 12th hour incidences out of 189 total. Ninety percent of all peak total oxidant concentrations occurred between the 12th and 14th hours, inclusive. July was the modal month for peak oxidant levels with 31 out of 189. On August 29, 1967 during the 7th hour a peak instantaneous NO_2 concentration of 13 pphm was attained. This was the 21st highest level recorded.

2. Frequency Distribution and Sample Statistics

The sample population of 8215 observations of total oxidant hourly average concentrations is skewed toward 0 pphm with sample mean at 4.57, sample standard deviation of 5.92 and modal value of 1.00 pphm. Ninety percent of the population values are less than 14 pphm. The value 14 falls 1.60 standard deviations from the mean.

3. Correlation and Regression Analysis

The highest correlation (in absolute value) of -.59 corresponded to the mixing height logarithmic average. This was followed by the value .5 for the CO logarithmic average. An 8-variable subset (CO, NO, mixing height, wind speed, pressure, temperature, relative humidity and sky cover) yielded a regression with a standard error of estimate of .085 and a shrunken multiple correlation coefficient of .78. The above standard error of estimate translates itself into the following 95-percent confidence band:

$$.68(OX_M) \leq (OX_R) \leq 1.48\ (OX_M)$$

4. Auto- and Cross-Correlation Analysis

All contaminant concentrations auto-correlation functions excepting total oxidant exhibited a marked decrease in the aforementioned persistence phenomenon. The subsequent cross-correlation analysis exhibited little serial cross-correlation between total oxidant concentration and the other pollutants, the largest in magnitude being -.43 for total hydrocarbons at lag 3. There was, however, good cross-correlation between total oxidant concentration and some of the meteorological pollutants: -.48 for mixing height at lag 2, .79 for temperature at lag 2, and .74 for wind speed at lag 3.

II. INDIVIDUAL CAMP CITIES

A. CHICAGO

1. Rank Order Analysis

The peak instantaneous level of total oxidant concentration of 16 pphm was reached on September 8, 1967 in the 12th hour. On 58 days a peak instantaneous concentration value of 7 pphm or more was measured. The hour in which the peak level occurred has a bimodal frequency distribution with primary mode at hour 15 and secondary mode at hour 13. Fifty-seven percent of all peak instantaneous total oxidant recordings fall between the hours of 12 and 16. June is the modal month of occurrence of high total oxidant levels, with 11 of 58 occurrences of oxidant levels of 7 or more pphm occurring in that month.

On September 8, 1967 at hour 7 an NO_2 concentration of 52 pphm was observed. This peak value of NO_2 concentration was the second highest measurement of the year, exceeded only by peak level of 63 pphm recorded on September 6, 1967 during the 6th hour.

2. Frequency Distributions and Sample Statistics

The frequency distribution of hourly average oxidant concentrations is strongly skewed to the left with mean of 2.93 pphm, modal value of 3 pphm and standard deviation of 2.02 pphm. In a total sample population of 5597 hourly average total oxidant observations, 95 percent of the observed values were less than 7 pphm. This value of 7 pphm is 2.04 standard deviations from the mean.

3. Correlation and Regression Analysis

A correlation analysis based on a restriction of the sample space to the 58 points where $(OX_M) \geq 7$ reveals:

- The highest correlation between dependent and independent variable is .389, corresponding to total hydrocarbon concentration.

- The next highest correlation of .326 corresponds to NO_2 concentration.

- The highest correlation in absolute value among the dependent variables and those corresponding to independent meteorological variables is -.261, associated with wind speed.

Utilizing information computed from the correlation analysis a regression analysis was carried out with the following results:

- The results of the regression were significant at the 99-percent level of confidence.

- The standard error of estimate for the complete regression was .088. This can be translated to mean that, with approximately 95-percent confidence, the regression estimate (OX_R) compiled by substituting observed values of the independent variable in the regression equation and taking the antilog of the result will satisfy:

$$.67(OX_M) \leq (OX_R) \leq 1.5(OX_M),$$

where (OX_M) is the observed peak hourly average total oxidant concentration.

- A smaller number of independent variables (NO, NO_2, total HC, temperature, and total sky cover) yields the smallest standard error of estimate (.0861) and largest shrunken multiple correlation coefficient (.523).

4. Auto- and Cross-Correlation Analysis

An auto-correlation analysis of 5 lags over a maximum of 96 possible hourly average rankings for four photochemical pollutants was carried out. The particular time sequence (June 2 to June 5) involved in the analysis was selected on the basis of high oxidant levels. Scanning the computer output it can be seen that:

- The auto-correlation functions of NO and total HC are very similar.

- The auto-correlation functions of NO_2 and OX match closely.

- There is fairly good correlation of approximately .7 between observed successive hourly values of NO and HC concentrations and the auto-correlation functions drop sharply for higher lags.

- There is very good correlation of approximately .9 between successive hourly values of NO_2 and OX. The auto-correlation functions drop gradually for higher lags.

The results of subsequent cross-correlations analysis were inconclusive. The highest (in absolute value) cross-correlation measured was .69 at lag zero for NO versus total HC. This result was in agreement with the correlation of .79 between the 3-hour logarithmic averages as observed in the correlation study.

B. CINCINNATI

1. Rank Order Analysis

The peak instantaneous level of total oxidant concentration of 19 pphm was reached on July 31, 1967 in the 13th hour. On 68 days a peak instantaneous concentration value of 7 pphm or more was measured. The hour in which the peak occurred has a unimodal frequency distribution with a modal value at 15 pphm. Sixty-six percent of all peak observed instantaneous values fall between the hours of 12 and 16. September is the modal month of occurrence of high total oxidant levels, with 15 out of 68 occurrences of observed high oxidant levels.

2. Frequency Distributions and Sample Statistics

The frequency distribution of hourly average oxidant concentrations is strongly skewed to the left with mean of 3.14 pphm and standard deviation 2.24 pphm. Over 94 percent of the observed sample population of 5310 hourly average total oxidant concentrations values are less than 7 pphm. This value of 7 pphm is 1.72 standard deviations from the mean of 3.14.

3. Correlation and Regression Analysis

The correlation analysis on samples for which maximum hourly average oxidant levels were greater than or equal to 7 was inconclusive. The highest correlation in absolute value was -.214 between oxidant and relative humidity.

The results of the subsequent full 10-variable regression analysis (9 independent variables) were significant at the 92-percent level of confidence. The best predictive results were obtained with a 5 independent variable subset (CO, NO, wind speed, temperature, relative humidity) regression. This regression was significant at the 99-percent level with a corresponding standard error of estimat of .097 and a shrunken multiple correlation coefficient of .40. Analogous to our results for Chicago, this "best" standard error of estimate yields, with about 95-percent confidence:

$$.61(OX_M) \leq (OX_R) \leq 1.63(OX_M),$$

where (OX_R) is predicted from the regression equation and (OX_M) is the corresponding observed peak hourly average total oxidant concentration taken from the restricted population of values greater than or equal to 7 pphm.

4. Auto- and Cross-Correlation Analysis

In the auto-correlation analysis a general similarity to the Chicago case can be observed, i.e.,

- The shapes of the NO and total HC auto-correlation curves agree fairly well.
- The same findings apply to NO_2 and total OX.
- Successive hour-to-hour correlations are high, with successive total oxidant values very highly correlated.

As for the cross-correlation analysis, it can be seen that total OX concentration is fairly negatively correlated with present and previous total hydrocarbons concentration. This last result seems, at first glance, to contradict the results of the correlation study. It must be remembered, however, that in that study logarithmic relationships were under investigation.

C. DENVER

1. Rank Order Analysis

The peak instantaneous level of total oxidant concentration of 20 pphm was recorded on August 14, 1967 during the 10th hour. On 48 days a peak oxidant value of 7 pphm or more was observed. The hour of peak instantaneous oxidant occurrence has a bimodal distribution with primary mode between 9 and 13. August is the modal month of occurrence for high oxidant levels, with 24 percent of such occurrences of peak values greater than or equal to 7 pphm.

2. Frequency Distribution and Sample Statistics

Consonant with results from Chicago and Cincinnati the frequency distribution of total OX concentration is strongly skewed to the left with mean of 2.83 pphm, a standard deviation of 2.03 pphm and a modal value of 2 pphm. The value 7 pphm exceeds 97 percent of the population of 36-7 values and is 2.06 sample standard deviations from the mean.

3. Correlation and Regression Analysis

The "best" correlations of the dependent variable were with the 3-hour logarithmic averages of NO and temperature. These were -.31 and .27, respectively. However, fairly good results were obtained in the regression study. A subset of 5 independent variables corresponding to NO, nonmethane HC, wind speed, temperature and total sky cover yielded a standard error of estimate of .089 and a shrunken multiple correlation coefficient of .66 at the 99.9-percent level of confidence. These figures correspond to the 95-percent confidence interval:

$$.67(OX_M) \le (OX_R) \le 1.5\ (OX_M)$$

4. Auto- and Cross-Correlation Analysis

Included in the auto-correlation analysis for comparison purposes are auto-correlations of three meteorological variables, wind speed, temperature, and relative humidity. As previously seen, among the photochemical contaminants total oxidant concentration is best correlated time-sequentially.

In the cross-correlation analysis a high negative correlation of -.82 is seen between present total oxidant levels and levels of NO_2 1 hour previously. Noting the small number of observations in the NO_2 sample, there is justifiably little confidence in this figure.

D. PHILADELPHIA

1. Rank Order Analysis

The maximum instantaneous value of total oxidant concentration of 17 pphm was attained on June 24, 1967 during the 16th hour. On 81 days a peak value of 7 pphm or greater was observed. The hour of peak occurrence has a unimodal frequency distribution with mode between 11 and 12. Fifty-five percent of all peak instantaneous oxidant concentration were recorded between the hours of 11 and 15. July is the modal month of incidence of high total oxidant concentration: 20 out of the total of 81 incidents were recorded in that month.

2. Frequency Distributions and Sample Statistics

The frequency distribution of hourly average oxidant concentrations is strongly left skewed with a mean of 2.63 pphm, mode of 2 pphm and standard deviation of 2.15 pphm. In a total sample population of 6134 observations, 94.46 percent of the population values were less than 7 pphm. The value 7 pphm is 2.00 sample standard deviations from the mean.

3. Correlation and Regression Analysis

The highest correlation between dependent and independent variables of .25 was attained for NO_2. This was followed by a value of .14 corresponding to the temperature variable. A subset of 8 variables (CO, NO, NO_2, nonmethane HC, wind speed, pressure, temperature and sky cover) yielded the best standard error of estimate of .095 and shrunken multiple correlation coefficient of .36. From this standard error of estimate the following 95-percent confidence level is derived:

$$.645(OX_M) \leq (OX_R) \leq 1.55(OX_M)$$

4. Auto- and Cross-Correlation Analysis

Case 1 (June 23 to June 25)

In this auto-correlation analysis it is seen that total oxidant and temperature auto-correlation functions are quite close in structure. Both exhibit very high correlations of over .9 at lag 0, .8 at a lag of 1 hour and thereafter dropping off slowly through values of approximately .8 for lag 2, .65 for lag 3, etc.

Case 2 (June 15 to June 18)

Once again it is noted that the hour-to-hour correlation of oxidant remains high for lags of 1 and 2 hours. Here the resemblance between the oxidant and temperature auto-correlation functions diminishes as the lag number grows.

Case 3 (August 26 to August 30)

Here the total oxidant correlation curve falls rather more rapidly than in the previous cases. The higher sample numbers indicate that these results may be viewed with somewhat higher confidence.

In the Case 3 cross-correlation analysis, the case with the highest sample numbers involved in computation of the cross-correlation, it can be observed that total oxidant is fairly well correlated (negatively) with present and preceding hourly values of NO and positively correlated with wind speed. This latter result may be indicative of contaminant transport phenomena.

E. ST. LOUIS

1. Rank Order Analysis

The highest instantaneous value of total oxidant concentration of 20 pphm was measured on June 30, 1967 during the 14th hour. On 119 days a peak value of 7 pphm or greater was measured. This hour of peak occurrence has a bimodal frequency distribution. The primary mode is at hour 12 with 22 occurrences. Fifty percent of all peak instantaneous averages occur between the hours of 10 and 15. July is the modal month of high oxidant levels with 24 and 119 or 20.2 percent of such recordings being recorded in July. It can be observed that a broad interval of months starting in April and ending in October contain almost 75 percent of the high oxidant days.

2. Frequency Distribution and Sample Statistics

The frequency distribution of hourly average oxidant concentrations is strongly left skewed with a mean of 3.44 pphm, mode of 2 pphm and a sample standard deviation of 2.29 pphm. In a total sample population, 94 percent of the values are less than 7 pphm. The value 7 pphm is 1.55 sample standard deviations from the mean.

3. Correlation and Regression Analysis

Case 1

The highest correlation in absolute value of -.46 in a sample of 39 corresponded to total oxidant and wind speed. The next highest value of -.26 was attained for wind speed. A subset of 4 variables (CO, NO, NO_2 and wind speed) yielded a regression significant at the 99.6-percent level in which the standard error of estimate was .062 and the shrunken multiple correlation coefficient was .54. Corresponding to the above sample standard error of estimate, the following 95 percent confidence interval was computed:

$$(.750OX_M) \leq (OX_R) \leq 1.33\ (OX_M)$$

This inequality is equivalent to saying that with probability of approximately .95 the relative error in predicting oxidant concentration from the regression formula will lie between -.25 and +.33.

Case 2

The sample of Case 1 was a 39 point subset of Case 2. In Case 2 there are 119 sample points corresponding to the 119 days of peak oxidant levels. For this case, the highest dependent-independent variable correlation of -.29 was between those corresponding to oxidant and wind speed. The next highest, .23, corresponded to NO_2. In the regression study a 4-variable subset (NO, NO_2, wind speed, and total sky cover) yielded a regression significant at the 99.40-percent level with a standard error of estimate of 0.92 and shrunken multiple correlation coefficient of .36. Corresponding to the above standard error of estimate is the 95-percent regression confidence interval:

$$.65(OX_M) \leq (OX_R) \leq 1.53(OX_M)$$

4. Auto- and Cross-Correlation Analysis (June 29 to July 2)

For lag numbers 0 through 5 based on samples of 89, 84, 82, 81, and 80, respectively, the corresponding auto-correlation of oxidants were 1, .91, .76, .58, .41, and .27. Here again is an example of the strong linear serial dependence of total oxidant concentrations.

The highest cross-correlation obtained was .54 between hourly average total oxidant concentration and NO_2 concentration 5 hours earlier.

F. WASHINGTON

1. Rank Order Analysis

The peak instantaneous value of 25 pphm for total oxidant was recorded on November 27, 1967 during the first hour. This also corresponds to the time of occurrence of the third highest instantaneous NO_2 level of 76 pphm. Obviously, the time of this particular event precludes an association with any photochemical mechanism. Further, the underlying data quality becomes highly suspect. On 79 days a peak instantaneous level of 7 pphm or greater was observed. The hour of peak occurrence has a bimodal shape with a questionably small tertiary mode at 23. The primary mode is at 12. The secondary mode is at 15. Seventy-two percent of all instantaneous total oxidant peak values occur between the 12th and the 16th hours, inclusive. July is the modal month of peak oxidant occurrence, with 18 out of 79 such occurrences taking place in that month.

2. Frequency Distributions and Sample Statistics

The frequency distribution of hourly average oxidant concentrations is skewed to the left with a mean of 2.57 pphm, a mode of 2 pphm and a standard deviation of 2.30 pphm. In a total sample of 7080, 94 percent of the recorded values are less than 7 pphm. The value 7 pphm lies 1.93 standard deviations to the right of the mean.

3. Correlation and Regression Analysis

The highest correlation of .48 was for the CO variable. This was followed by a correlation of .33 for NO and -.25 for total sky cover. A 6-variable subset (CO, NO, pressure, temperature, relative humidity, and total sky cover) yielded a regression significant at the 99.999-percent level in which the standard error of estimate was .099 and the shrunken multiple correlation coefficient was .56. Correspponding to the above sample standard error of estimate, the following 95 percent confidence band was derived:

$$.63(OX_M) \leq OX_R) \leq 1.58(OX_M)$$

4. Auto- and Cross-Correlation Analysis

Case 1 (first high oxidant episodic sequence: (July 26 to 28)

The total oxidant auto-correlation function exhibits the previously discussed properties. That is, very high correlation of .93 at lag 1, gradually decreasing through values of .82 at lag 2, .63 at lag 3, etc. The other photochemical pollutants for which data are available have fair to good correlations at lag 1 but drop rapidly for higher lag numbers. The largest total oxidant cross-correlation (in absolute value) of -.58 occurs at lag 1 for NO.

Case 2 (low oxidant sequence: (November 17 to 21)

The total oxidant autocorrelation function has values of .85, .66, .47, .27, and .09 for lags 1, 2, 3, 4, and 5, respectively. The highest auto-correlation of .93 at lag 1 is for NO_2. The highest cross-correlation of .54 occurred between total oxidant concentration and wind speed.

Case 3 (second high episodic sequence: (November 25 to 27)

This appears to be a highly atypical episode. It is in this sequence of days that several instantaneous peaks occur during the evening: that is, three peak oxidant levels are observed during the 23rd hour. Without a minutely detailed investigation of the environmental circumstances, the performance status of the instrumentation, etc., it would be unwise to put forth as valid even the most cursory interpretation.

APPENDIX II

MATHEMATICAL DESCRIPTION OF THE MODEL

METEOROLOGICAL MODULE EQUATIONS

1.0 INTRODUCTION

The meteorological module computes the values of six trajectory point output variables and their time derivatives as a function of time and trajectory position inputs. Wind velocity x and y components, temperature, pressure, relative humidity, weather cover and mixing depth and their time derivatives are estimated via weighted inverse distance squared interpolations on time-correspondent values among all "permissible" meteorological stations. Permissible stations are those which lie together with the trajectory point on one side of each line segment of a set of predefined polygonal barriers. Given height above sea level, temperature, and the x and y components of wind velocity, the module derives a mixing depth and a mixing depth time derivative.

The mixing height is computed by passing a straight line of slope -.00986 (the dry adiabatic lapse rate) through the trajectory height-temperature point and determining the abscissa of its intersection with one of two polygonal temperature-versus-height radiosonde curves. The appropriate curve is selected on the basis of input time.

The mixing height derivative is computed as a linear function of the temperature and height-above-sea-level derivatives, which in turn are derived from interpolating equations for the temperature and height and the interpolating equations for the x and y components of velocity. The mixing depth and mixing depth derivative are computed by subtracting interpolated height-above-sea-level and derivative from mixing height and its derivative

2.0 DERIVATIONS

2.1 Definition of the Barrier and Permissible Stations

Each barrier is defined by an integer N_B, which is one greater than the number of barrier sides, and a sequence of points (x_i, y_i), $i=1, 2, \ldots, N_B$, with each consecutive pair of points defining a side of the barrier. Let (x_o, y_o) and (x_s, y_s) be, respectively, the coordinate of the trajectory point and a given station. Let $m=(y_s-y_o)/(x_s-x_o)$, $b=y_o-mx_o$ be the slope and y the intercept of the line joining the trajectory point to the station. For each $i=1, 2, \ldots, N_B-1$ let

$$m_i=(y_{i+1}-y_i)/(x_{i+1}-x_i)$$

$$b_i = y_i - m_i x_i$$

$$\lambda_i = \frac{y_s - m_i x_i - b_i}{m_i (x_o - x_s) - (y_o - y_s)} \qquad (2\text{-}1)$$

$$\mu_i = \frac{y_{i+1} - m x_{i+1} - b}{m(x_i - x_{i+1}) - (y_i - y_{i+1})} \qquad (2\text{-}2)$$

A station located at (x_s, y_s) is said to be permissible if, and only if, for each $i=1, 2, . . ., N_B - 1$ either $\lambda_i \geq 0, \lambda_i \geq 1, \mu_i \leq 0$ or $\mu_i \geq 1$.

B. INTERPOLATION OF METEOROLOGICAL VARIABLES

Let (x_j, y_j) be the coordinates of each permissible station $(j=1,2,...N_p)$. Let, $d_1, d_2, d_3, ..., d_{N_p}$ be the distance from these stations to the trajectory point and let $\dot{x}_1, \dot{x}_2, ..., \dot{x}_{N_p}$ be, for example, the corresponding set of observed x components of wind velocity. The x component of wind velocity, $\dot{x}_o$, at the trajectory point is estimated according to:

$$\dot{x}_o = \sum_{j=1}^{N_p} \dot{x}_j / d_j^{\,2} \qquad (2\text{-}2.1)$$

Each of the five remaining trajectory point variables is estimated by the corresponding analogue to equation (2-2.1).

The time derivative, p_o, of, say pressure, is computed according to

$$\dot{p}_o = 2 \left\{ B p_o - \sum_{j=1}^{N_p} p_j \left[(x_o - x_j)\dot{x}_o + (y_o - y_j)\dot{y}_o \right] / d_j^4 \right\} / A \qquad (2\text{-}2.2)$$

where

$$A = \sum_{j=1}^{N_p} 1/d_j^2 \text{ and } B = \sum_{j=1}^{N_p} \left[(x_o - x_j)\dot{x}_o + (y_o - y_j)\dot{y}_o \right] / d_j^4 \qquad (2\text{-}2.3)$$

Each of the remaining trajectory time derivatives is estimated analagous to (2-2.2).

C. COMPUTATION OF MIXING HEIGHT AND MIXING HEIGHT DERIVATIVE

Given the interpolated values (z_o, T_o) of height above sea level and temperature at our trajectory point, the module selects the appropriate A.M. or P.M. radiosonde curve depending on the value t_o. Each of these curves is defined by an integer $N_{a.m.}$ or $N_{p.m.}$ and a sequence of points (z_k, T_k) $k=1,2,\ldots N_{a.m.(p.m.)}$.

The mixing height, h_m, is computed according to:

$$h_m = \frac{T_o - T_k + m_k z_k - \alpha z_o}{m_k - \alpha} \tag{2-3.1}$$

where k is the first integer such that $1 \leq k < N_{a.m.(p.m.)}$, $z_k < h_m < z_{k+1}$, $z_o \leq h_m$, $m_k = (T_{k+1} - T_k)/(z_{k+1} - z_k)$, and $\alpha = -.00986$ °C/meter.

The mixing height derivative, $\dot{h}_m$, is computed according to:

$$\dot{h}_m = (\dot{T}_o - \dot{z}_o)/(m_k - \alpha)$$

III. Symbol Glossary and Units

$\dot{x}_o$ [meters/minute] = x component of wind velocity

$\dot{y}_o$ [meters/minute] = y component of wind velocity

T_o [degree centigrade (°C)] = temperature

p_o [millibar] = pressure

H_o [dimensionless] = relative humidity

w_o [dimensionless] = cloud cover

z_o [meters] = height-above-sea level

h_m [meters] = mixing height

$\dot{h}_m$ [meters/minute]

$\dot{T}_o$ [°C/minute]

$\dot{P}_o$ [millibars/minute]

$\dot{H}_o$ [1/minutes]

$\dot{w}_o$ [1/minutes]

$\dot{z}_o$ [meters/minute]

ULTRAVIOLET IRRADIANCE MODULE EQUATIONS

1.0 INTRODUCTION

The basic physical hypotheses underlying this module's computations have been taken almost directly from [1]. Our departure is in the formulation of a total irradiance equation which takes into account albedo and weather effects and which reduces to a standard form (see equation II-29 of [1]) when the cloud cover and albedo are both zero. Thus, our final formulation (see equation 2-7) will differ from any developed on the basis of equation (II-38) of [1]. The input to the module is the time t_o, the height above sea level of the trajectory point, z_o, the relative humidity at the trajectory point H_o, the corresponding atmospheric pressure p_o, the mixing depth, h_m, the weather cover, w_o, and the average concentration of NO_2, $\bar{C}_{NO_2}$, in the column. The module's output is the specific absorption rate of NO_2, k_{NO_2}.

2.0 DERIVATIONS

As a function of the time of day, t_o (Pacific Standard Time), a value of the solar zenith angle θ, is interpolated from a table derived from the equinox curve of Figure 2. in Chapter II of [1]. The air mass, m, is interpolated as a function of θ in Table 2 of [1].

Depending on an input cloud-type parameter, a value of average fraction of radiation transmitted, β, is interpolated in Table 10 of [1]. For each wavelength band of 100Å in a wavelength region of $3000\text{Å} \le \lambda \le 4000\text{Å}$, the molecular scattering coefficient $(s_{m\lambda})_o$ is selected from Table 3 of [1]. From equation (II-9) of [1], the transmissivity relative to molecular scattering, $T_{m\lambda}$, may be computed from the formula

$$\log_{10} T_{m\lambda} = -(s_{m\lambda})_o \frac{p_o m}{1013.250} \qquad (2\text{-}1)$$

where p_o is the interpolated pressure in millibars.

The transmissivity relative to particle scattering, $T_{p\lambda}$, may be computed from the formula (II-11) of [1] (with λ in microns)

$$\log_{10} T_{p\lambda} = -(3.75\text{x}10^{-3}\lambda^{-2}W + 3.5\text{x}10^{-2}\lambda^{-.75}d)m \qquad (2\text{-}2)$$

where W is the amount of precipitable water vapor in the atmosphere, measured vertically above the trajectory point, computed as in equation (II-2) of [1], in units of centimeters, according to:

$$W = 1.722 \times 10^{-1} P_W 10^{-(z_o/22{,}000)} \quad (2\text{-}3)$$

Where P_W is the partial pressure in millibars of water vapor at the trajectory point. P_W is interpolated from a vapor pressure table in [2], and d is a dimensionless parameter of preset nominal value 1.

The ozone absorption coefficient α_λ[meters^{-1}] is interpolated from Table 5 and the transmissivity of ozone, $T_{a\lambda}$, as in equation (II-13) of [1], may be computed from

$$\log_{10} T_{a\lambda} = -\alpha_\lambda (O_3) m \quad (2\text{-}4)$$

where (O_3) is a preset parameter of nominal value 2.2×10^{-3}[meters] (of ozone).

The mean solar spectral irradiance, $I_{0\lambda}$, is selected from Table 1 and the direct and sky radiation $I_{d\lambda}$ and $I_{s\lambda}$ are computed from equations (II-15) and (II-16):

$$I_{d\lambda} = T_{s\lambda}\, T_{a\lambda}\, I_{0\lambda} \cos\theta \quad (2\text{-}5)$$

$$I_{s\lambda} = g(1-T_{s\lambda}) T_{a\lambda} I_{0\lambda} \cos\theta \quad (2\text{-}6)$$

where $T_{s\lambda} = T_{m\lambda} T_{p\lambda}$ and g is a preset dimensionless parameter of nominal value .5.

Following the development from equations (II-17) through (II-28) of [1] and taking average weather cover and an average albedo effect into account, we obtain the formula for the average rate of absorption per unit pollutant$_o$ column volume for direct and sky radiation over a wavelength band of 100A centered at wavelength λ, $I_{a\lambda}$:

$$I_{a\lambda} = \frac{\left\{1+a\right\}\left\{I_{d\lambda}(1-w_o)(1-10^{-\alpha_\lambda \bar{C}_{NO_2} h_m \sec\theta}) + \left[\beta w_o I_{d\lambda} + (1-w_o+\beta w_o) I_{s\lambda}\right](1-10^{-2\alpha_\lambda \bar{C}_{NO_2} h_m})\right\}}{h_m}, \quad (2\text{-}7)$$

where a is the albedo (preset nominal value of .235), w_o is the weather cover, and $\bar{C}_{NO_2}$ is the average column concentration of NO_2. α_λ now refers to NO_2.

Finally, the specific absorption rate of NO_2, k_{NO_2} derived from equations (II-31) and (II-32) of [1] is computed as:

$$k_{NO_2} = \frac{1}{7.2} \times 10^{-16}\left(\frac{273+T_o}{p_o\bar{C}_{NO_2}}\right)\sum_{\lambda=3000\text{Å}}^{4000\text{Å}} I_{a\lambda} \qquad (2\text{-}8)$$

3. UNITS

All lengths are in meters.

Time is in minutes.

Temperature is in ^{o}C.

All pressures are in millibars.

$I_{O\lambda}$ are in photons meters^{-2} minutes^{-1}(100Å)$^{-1}$.

$\bar{C}_{NO_2}$ is in pphm.

k_{NO_2} is in minutes^{-1}.

w_o is dimensionless.

β is dimensionless.

4. REFERENCES

[1] P. A. Leighton, Photochemistry of Air Pollution, Academic Press, New York, 1961.

[2] Handbook of Physics and Chemistry.

KINETICS MODULE EQUATIONS

1.0 INTRODUCTION

We first characterize an abstract k step $-N_\sigma$ species constant mass, constant volume chamber photochemical mechanism. As a consequence of this characterization, using standard principles of chemical kinetics, we can write, in compact notation, the differential equations of species concentration for the constant volume, constant mass situation. Next, we expand our conceptual framework to the chemical kinetics of the contents of a pollutant column whose motion over a time-varying field of urban emission sources induces variations in average column temperature, volume mass, etc. This is accomplished by adding a series of appropriate first order pertubation terms to the species concentration time derivatives. It is to be emphasized that the step number and number of species characterizing our imbedded kinetic mechanism are limited only by computer storage and computation time considerations. For this reason we are utilizing the IBM 360-67, a high-speed, large storage computer, in conjunction with an auxiliary FORTRAN system whose function is to derive a set of differential equations from a corresponding set of photochemical equations. Thus, we have complete flexibility in step number, species number and, more importantly, the photochemical equations themselves.

The inputs to the module are the outputs of the weather, diffusion, and ultraviolet irradiance modules.

2.0 DERIVATIONS

An abstract k-step, N_σ-species, constant-volume, constant-mass photochemical mechanism is characterized by (i) a binary valued kxN_σ matrix B whose (i, j) element, b_{ij}, is 1 if and only if the jth species appears as a reactant in the i^{th} (elementary) step; (ii) an integer valued kxN_σ species conservation matrix, P, whose (i, j) element, P_{ij}, is the number of molecules of species j produced ($p_{ij} \geq 0$) or consumed ($p_{ij} < 0$) in the ith step; (iii) a K-element vector F of reaction rate factors k_j, $j = 1, 2, \ldots K$; and (iv) a N_σ- element vector, C_o, of initial concentrations, $C_\ell(0)$, $\ell = 1, 2, \ldots, N_\sigma$. From the above definitions and elementary considerations of chemical kinetics, we may formulate the following set of differential equations:

$$\dot{C}_i(t) = \sum_{j=i}^{k} p_{ji} k_j \left(\prod_{\left\{\ell : b_{j\ell=1}\right\}}^{N_\sigma} C_\ell(t) \right), \tag{2-1}$$

$$C_i(0) = C_{io}$$

$$(i = 1,2,\ldots,N_\sigma)$$

or, in matrix-vector form:

$$\dot{C}(t) = P^T R(t) \tag{2-2}$$

$$C(0) = C_o,$$

where

$$\dot{C}(t) = \begin{bmatrix} \dot{C}_1(t) \\ \dot{C}_2(t) \\ \dot{C}_3(t) \\ \cdot \\ \cdot \\ \cdot \\ \cdot \\ \dot{C}_{N\sigma}(t) \end{bmatrix}, \tag{2-3}$$

$$R(t) = \begin{bmatrix} k_1 \prod\limits_{\{\ell : b_{1\ell}=1\}} C_\ell(t) \\ \vdots \\ k_K \prod\limits_{\{\ell : b_{K\ell}=1\}} C_\ell(t) \end{bmatrix}, \qquad (2\text{-}4)$$

and P^T is the transpose of P.

Taking equation (2-2) as our starting point, we permit F to be time-varying (i.e., k_j are replaced by $k_j(t)$) and add first order perturbations due to stationary sources, $\dot{C}_S(t)$, traffic sources, $\dot{C}_T(t)$, and the rate of change of column volume, $\dot{C}_V(t)$, to derive the pollutant column concentration differential equations:

$$\dot{C}(t) = P^T R(t) + \dot{C}_S(t) + \dot{C}_T(t) + \dot{C}_V(t), \qquad (2\text{-}5)$$

$$C(0) = C_o$$

where

$$\dot{C}_V(t) = \begin{cases} 0 \text{ if } h_m \leq 0 \\ \dfrac{-\dot{h}_m}{h_m} C(t) \text{ if } h_m > 0 \end{cases} \qquad (2\text{-}6)$$

3.0 UNITS

All concentrations are in parts per hundred million. Concentration rates are in pphm/minute. h_m (mixing depth) is in meters $\dot{h}_m$ (mixing depth time derivative) is in meters/minute.

TRAFFIC MODULE EQUATIONS

1. INTRODUCTION

We first note that the present module represents a "first pass" attempt to provide working traffic emission inputs for the photochemical simulation model. As such a prototype it is necessarily based on a set of simplifying assumptions leading to a compact formulation which, nevertheless, takes into account such parameters as total daily vehicle mileage, area population ratios, emission rates, diurnal traffic variations and local meteorology.

In characterizing the module, the Los Angeles Basin is subdivided into a grid system of 784 equal 4-square-mile squares corresponding to a 56- by 56-mile square total area. To each of these grid areas is assigned a daily vehicle mileage ratio representing the ratio of the daily mileage in this subarea to the total daily mileage. The module is further characterized by a set of pollutant emission rates given in grams per mile, a traffic density function, and a total vehicle mileage figure. The emission rates are computed from published emission factor data by an auxiliary preprocessing program. The inputs to the module are the time, t, the position of the pollutant column, (x,y), the temperature, T_o, the pressure, p_o, and the mixing-depth, h_m, at (x,y) and their corresponding time derivatives, $\dot{T}_o$, $\dot{p}_o$, and $\dot{h}_m$.

The module's output is the vector of concentration rates, $\dot{c}_T$, due to traffic.

2. DERIVATIONS

Given the position (x,y) (in miles) such that $16 \leq x < 72$ and $0 \leq y < 56$, the projection of the column centroid falls in grid sub area i with ratio, r_i, where i is computed according to:

$$i = \left[\frac{x}{2}\right] - 7 + 28\left[\frac{y}{2}\right] \tag{2-1}$$

where [z] = integer part of z.

Let L (a preset constant of nominal value 1.2×10^7) be the daily vehicle mileage. Let $\bar{E}_j$ and m_j be, respectively, the average emission rates (grams/mile) and the gram molecular weight of the jth pollutant ($j=1,2,\ldots,N_\sigma$).

Then, assuming uniform areal distribution, the number of moles of the jth pollutant emitted by traffic in a 1 meter^2 subarea of the ith grid up to time t, $n_j(t)$, is given by:

$$n_j(t) = 9.64\text{x}10^{-8} \frac{r_i L\bar{E}_j}{m_j} \int_0^t f(s)ds \tag{2-2}$$

where (see Figure II-1)

$$f(t) = \begin{cases} \alpha \text{ if } 0 \leq t < 6 \\ \alpha + \frac{\beta}{2}(t-6) \text{ if } 6 \leq t < 8 \\ \alpha + \beta - \frac{(\beta - 2\alpha)}{2}(t-8) \text{ if } 8 \leq t < 10 \\ 3\alpha \text{ if } 10 \leq t < 16 \\ 3\alpha + \beta - \frac{(\beta + \alpha)}{2}(t-18) \text{ if } 18 \leq t < 20 \\ \alpha[2 - \frac{1}{4}(t-20)] \text{ if } 20 \leq t < 24 \end{cases} \tag{2-3}$$

(α is a preset constant of nominal value 1/85 and β is computed as $\beta = (1-47\alpha)/4$).

From the ideal gas law the number of moles of air, $n(t)$, in a column 1 meter^2 in cross-sectional area and h_m meters in height is computed as:

$$n(t) = p_o h_m / .0832(T_o + 273) \tag{2-4}$$

The concentration in pphm, c_{jT}, of the jth pollutant due to traffic emissions (assuming a constant zero loss function in this version of the module) is computed as:

$$c_{jT} = \frac{10^8 n_j(t)}{n(t)} = \left[.802 r_i L E_j (273 + T_o)/m_j p_o h_m\right] \int_0^t f(s)ds \qquad (j=1,2,\ldots N_\sigma) \quad . \tag{2-5}$$

Differentiating with respect to time, we obtain the module output concentration rate, $\dot{c}_{jT}$, as

$$\dot{c}_{jT} = (.802 r_i L\bar{E}_j / p_o h_m) \left\{ \frac{(T_o + 273) f(t)}{60} + \left[\frac{p_o h_m \dot{T}_o - (T_o + 273)(\dot{p}_o h_m + p_o \dot{h}_m)}{p_o h_m} \right] \int_0^t f(s)ds \right\} \tag{2-6}$$

$$(j=1,2,\ldots,N_\sigma) \quad .$$

DIURNAL TRAFFIC VOLUME CURVE

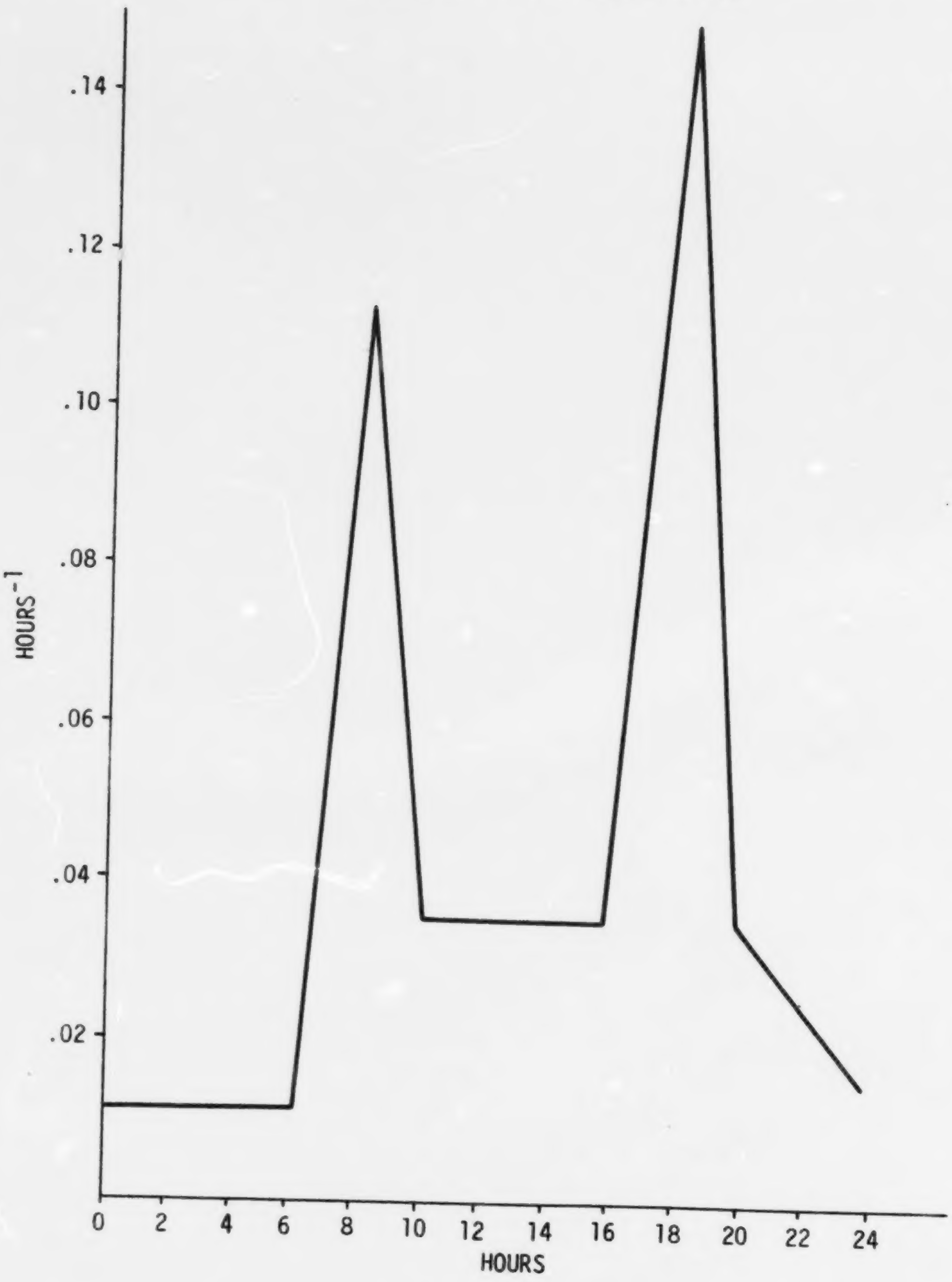

FIGURE II-I.

3. UNITS

T_o [°C]

h_m [meters]

p_o [millibars]

$\dot{T}_o$ [°C/min.]

$\dot{h}_m$ [meters/min.]

$\dot{p}_o$ [millibars/min]

r_i [dimensionless]

L [miles]

$\bar{E}_j$ [grams/mile]

f(t) [1/hours]

STATIONARY STACK SOURCE (DIFFUSION) EQUATIONS

1.0 INTRODUCTION

The Stationary Stack Source or Diffusion module computes the contribution to the concentration derivatives of NO and NO_2 in a pollutant column with position (x_o, y_o) and velocity $(\dot{x}_o, \dot{y}_o)$ due to presence of upwind stationary stack sources. The set of such sources is characterized by an integer N_s and a N_sx9 matrix of stack parameters $(x_s, y_s, z_s, H_s, D_s, V_s, T_s, P_s, Q_s)$, s-1,2,..,$N_s$, where (x_s, y_s) is the position of the stack, z_s the height of its base above sea level, H_s its height, D_s its diameter, V_s the exhaust speed of its gas, T_s its inside temperature, P_s its ambient atmospheric pressure, and Q_s its emission rate of NO. Module computations are based on the assumption of small variation in wind velocity both spatially and temporally for "nearby" upwind stack sources. This supposition allows us to use the standard stationary source diffusion equations to be found, for example, in reference (1). It is to be noted that such a hypothesis serves to emphasize the "credible episode" nature of the photochemical modle.

The inputs to the module are column position $\underline{X}$, column velocity $\underline{\dot{X}}$, pressure p_o, temperature, T_o, mixing depth, h_m, height above-sea-level, z_o, the corresponding time derivatives and the time t_o. The output is total stationary source conce concentration derivatives for NO and NO_2.

2.0 DERIVATIONS

Let $\underline{X}=(x_o, y_o)$ and $\underline{\dot{X}}=\dot{x}_o, \dot{y}_o)$ be the position and velocity vectors of a pollutant column. For each stack source s=1,2,...,N_s whose position vector $\underline{X}_s=(x_s, y_s)$ satisfies $(\underline{X}-\underline{X}_s).\underline{\dot{X}}\geq 0$, the module determines the corner of the column base nearest the stack from among the four candidates: $\underline{X} \pm \frac{1}{2s_o}(\dot{x}_o, \dot{y}_o) \pm \frac{1}{2s_o}(\dot{y}_o, -\dot{x}_o)$. Denoting this nearest corner position as $\underline{X}^s$, the downwind distance from the stack to the nearest corner, ξ_s, is computed according to:

$$\xi_s = (\underline{X}^s - \underline{X}_s) \cdot \underline{\dot{X}} / s_o \; ,$$

where

$$s_o = \| \underline{\dot{X}} \| = \sqrt{\dot{x}_o^2 + \dot{y}_o^2} \qquad (2\text{-}1)$$

The cross-wind distance from the centerline, η_s, is computed according to:

$$\eta_s = \sqrt{\| \underline{X}^s - \underline{X}_s \|^2 - \xi_s^2} \tag{2-2}$$

Following (1), from equation (3.1) on page 5 we may compute the mass contribution of NO_x, M_s from stack s to a column of unit square cross sectional areas and height h_m (mixing depth) according to:

$$M_s = \int_{x=\xi}^{\xi+1} \int_{y=\eta}^{\eta+1} \int_{z=z_o}^{\bar{h}_m} \chi_s(x,y,z)\,dz\,dy\,dx = \tag{2-3}$$

$$\frac{Q_s}{s_o} \int_{\xi}^{\xi+1} \left\{ \mathrm{erf}\left[\frac{\eta+1}{\sigma_y(x)}\right] - \mathrm{erf}\left[\frac{\eta}{\sigma_y(x)}\right] \right\} \left\{ \mathrm{erf}\left[\frac{\bar{h}_m - H_{sv}}{\sigma_z(x)}\right] + \mathrm{erf}\left[\frac{h_m + H_{sv}}{\sigma_z(x)}\right] - \mathrm{erf}\left[\frac{z_o - H_{sv}}{\sigma_z(x)}\right] - \mathrm{erf}\left[\frac{z_o + H_{sv}}{\sigma_z(x)}\right] \right\} dx \tag{2-4}$$

where $\bar{h}_m = h_m + z_o$ (mixing height) and

$$\chi_s = \frac{Q_s}{2\Pi\sigma_y(x)\sigma_z(x)s_o} \left\{ \exp\left[-y^2/2\sigma_y^{\,2}(x)\right] \right\} \left\{ \exp\left[-(z-H_{sv})^2/2\sigma_z^{\,2}(x)\right] + \exp\left[-(z+H_{sv})^2/2\sigma_z^{\,2}(x)\right] \right\}. \tag{2-5}$$

Denoting the molar contribution of NO and NO_2 from stack s to the column as n_{1s} and n_{2s}, respectively, assuming that these molar contributions are proportional to the existing column concentrations C_{NO} and C_{NO_2}, and taking into account the conservation of mass, we have:

$$n_{1s} + n_{2s} = M_s/30 \tag{2-6}$$

$$-C_{NO_2} n_{1s} + C_{NO} n_{2s} = 0,$$

or, solving for n_{1s}, and n_{2s}:

$$n_{1s} = \frac{C_{NO}}{30(C_{NO}+C_{NO_2})} M_s \tag{2-7}$$

$$n_{2s} = \frac{C_{NO_2}}{30(C_{NO}+C_{NO_2})} M_s$$

From the ideal gas law, we compute the number of moles of air in the column, n, according to:

$$n = \frac{1}{1013.25} \frac{P_o h_m}{RT_o} , \tag{2-8}$$

and we compute the total upwind stacks to column concentration contributions of NO and NO_2, $C_{NO,S}$ and $C_{NO_2,S}$, respectively, as:

$$C_{NO,S} = \frac{10^8}{n} \sum_{\left\{s:\, (\underline{X}-\underline{X}_s)\cdot\dot{\underline{X}}>0\right\}} n_{1s} \tag{2-9}$$

$$C_{NO_2,S} = \frac{10^8}{n} \sum_{\left\{s:\, (\underline{X}-\underline{X}_s)\cdot\dot{\underline{X}}>0\right\}} n_{2s}$$

or

$$C_{NO,S} = 2.77\text{x}10^5 U_{NO} VW \tag{2-10}$$

$$C_{NO_2,S} = 2.77\text{x}10^5 U_{NO_2} VW,$$

where

$$U_{NO} = C_{NO}/(C_{NO}+C_{NO_2})$$

$$U_{NO_2} = C_{NO_2}/(C_{NO}+C_{NO_2})$$

$$V = (T_o+273)/p_o h_m$$

$$W = \sum_{\left\{s:(\underline{X}-\underline{X}_s)\cdot\underline{\dot{X}}>0\right\}} M_s$$

Differentiating with respect to time:

$$\dot{C}_{NO} = 2.77\text{x}10^5(\dot{U}_{NO}VW+U_{NO}\dot{V}W+U_{NO}V\dot{W}) \qquad (2\text{-}11)$$

$$\dot{C}_{NO_2} = 2.77\text{x}10^5(\dot{U}_{NO_2}VW+U_{NO_2}\dot{V}W+U_{NO_2}V\dot{W}),$$

where

$$\dot{U}_{NO} = (C_{NO_2}\dot{C}_{NO}-C_{NO}\dot{C}_{NO_2})/(C_{NO}+C_{NO_2})^2, \qquad (2\text{-}12)$$

$$\dot{U}_{NO_2} = -\dot{U}_{NO}$$

$$\dot{V} = [\dot{T}_o p_o h_m-(T_o+273)(\dot{p}_o h_m+p_o\dot{h}_m)]/(p_o h_m)^2$$

$$\dot{W} = \sum_{\left\{s:(X-X_s)\cdot\dot{X}\geq 0\right\}} \dot{M}_s \text{ , and}$$

$$\dot{M}_s = Q_s\left\{\left\{\left[\text{erf}\left(\frac{\eta+1}{\sigma_y(x)}\right)-\text{erf}\left(\frac{\eta}{\sigma_y(x)}\right)\right]\left[\text{erf}\left(\frac{\bar{h}_m-H_{sv}}{\sigma_z(x)}\right)+\text{erf}\left(\frac{\bar{h}_m+H_{sv}}{\sigma_z(x)}\right)-\text{erf}\left(\frac{z_o-H_{sv}}{\sigma_z(x)}\right)-\text{erf}\left(\frac{z_o+H_{sv}}{\sigma_z(x)}\right)\right]\right\}\right\}_{x=\xi}^{x=\xi+1}$$

$$+\frac{Q_s}{\sqrt{2\pi}s_o}\int_{\xi}^{\xi+1}\left[\text{erf}\left(\frac{\eta+1}{\sigma_y(x)}\right)-\text{erf}\left(\frac{\eta}{\sigma_y(x)}\right)\right]\left\{\dot{\bar{h}}_m\left\{\exp\left[-\frac{(\bar{h}_m-H_{sv})^2}{2\sigma_z^2(x)}\right]+\exp\left[-\frac{(\bar{h}_m+H_{sv})^2}{2\sigma_z^2(x)}\right]\right\}\right.$$

$$\left.-\dot{z}_o\left\{\exp\left[-\frac{(z_o-H_{sv})^2}{2\sigma_z^2(x)}\right]+\exp\left[-\frac{(z_o+H_{sv})^2}{2\sigma_z^2(x)}\right]\right\}\right\}\frac{dx}{\sigma_z(x)},$$

where $\dot{h}_m$ is the mixing height derivative, $\dot{z}_o$ is the time derivative of height above-sea-level, $\dot{T}_o$ is the column temperature derivative, $\dot{p}_o$, is the column pressure derivative, erf (U) = $\frac{1}{\sqrt{2\pi}}\int_{-\infty}^{U}\exp\left(\frac{-u^2}{2}\right)du$, $\sigma_y(x)$ and $\sigma_z(x)$ are interpolated, depending on a stability parameter, from two of the appropriate graphs on page 8 and 9 of (1), and

$$H_{sv} = z_s+H_s+\frac{V_s}{s_o}D_s\left[1.5+2.68x10^{-3}P_sD_s\left(T_s-T_a\right)/\left(T_s+273\right)\right] \cdot \qquad (2\text{-}13)$$

In equation (2-13) T_a and P_s, the ambient atmospheric temperature and pressure, respectively, are interpolated via the weather module. It is also assumed that $\dot{H}_{sv} = 0$.

3. UNITS

All lengths are in meters.

Speeds are in meters/minute.

Temperature is in °C.

Pressure is in millibars.

Emission rates are in pphm/minute.

T_o is in °C/min.

p_o is in millibars/minute

4. REFERENCE

(1) Workbook of Atmospheric Dispersion Estimates, U. S. Department of Health, Education and Welfare--Public Health Service--Consumer Protection and Environmental Health Service.